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Robert W. Talbot
Anders W. Andren

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Madison, WI 53706

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In a lake system where atmospheric input greatly exceeds other source inputs, the atmospheric supply, water column transport, and sediment accumulation should be coupled. This research examined the exchange of lead between these compartments. The approach was to use Pb-210 as a natural tracer to provide experimental evidence concerning the movement of lead between various compartments, thereby linking the geochemical regime of lead in an integrated lake system. The investigation was conducted in Crystal Lake, Wisconsin, an oligotrophic, non-calcareous, seepage lake located in a semi-remote, heavily forested area of north-central Wisconsin. The atmosphere serves as the principal route for transport of material to the lake. Stable Pb concentrations in the water column are of the order of 200 ng/kg. At least 85% of the atmospheric input of Pb and Pb-210 to Crystal Lake occurs by wet deposition. The dynamics of lead transport from the atmosphere to the lake surface and through the water column were studied in a manner such that observations of spatial and temporal variability include seasonal effects. The non-steady-state input and removal processes necessitate this type of approach if a realistic description of geochemical regimes in lakes is to be developed.

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Wisconsin Power Plant Impact Study

by

Robert W. Talbot
and
Anders W. Andren

Grant No. R806878-01-06

Project Officer
Gary E. Glass
Environmental Research Laboratory-Duluth
Duluth, Minnesota

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FOREWORD

The U.S. Environmental Protection Agency (EPA) was designed to coordinate our country's efforts toward protecting and improving the environment. This extremely complex task requires continuous research in a multitude of scientific and technical areas. Such research is necessary to monitor changes in the environment, to discover relationships within that environment, to determine health standards, and to eliminate potentially hazardous effects.

One project, which the EPA is supporting through its Environmental Research Laboratory in Duluth, Minnesota, is the study "The Impacts of Coal-Fired Power Plants on the Environment. This interdisciplinary study, centered mainly around the Columbia Generating Station near Portage, Wis., involves investigators and experiments from many academic departments at the University of Wisconsin and is being carried out by the Environmental Monitoring and Data Acquisition Group of the Institute for Environmental Studies at the University of Wisconsin-Madison. Several utilities and State agencies are cooperating in the study: Wisconsin Power and Light Company, Madison Gas and Electric Company, Wisconsin Public Service Corporation, Wisconsin Public Service Commission, and Wisconsin Department of Natural Resources.

The research presented in this report examined the exchange of lead between the atmosphere and a lake system. The approach was to use PB-210 as a natural tracer to provide experimental evidence concerning the movement of lead between various compartments, thereby linking the geochemical regime of lead in an integrated system.

Norbert A. Jaworski
Director
Environmental Research Laboratory
Duluth, Minnesota

ABSTRACT

In a lake system where atmospheric input greatly exceeds other source inputs, the atmospheric supply, water column transport, and sediment accumulation should be coupled. This research examined the exchange of lead betwen these compartments. The approach was to use Pb-210 as a natural tracer to provide experimental evidence concerning the movement of lead between various compartments, thereby linking the geochemical regime of lead in an integrated lake system.

The investigation was conducted in Crystal Lake, Wisconsin, an oligotrophic, non-calcareous, seepage lake. The lake has a surface area of 31 ha and a maximum depth of 21 m. Crystal Lake is located in a semi-remote, heavily forested area of north-central Wisconsin. The atmosphere serves as the principal route for transport of material to the lake. Stable Pb concentrations in the water column are of the order of 200 ng/kg.

At least 85% of the atmospheric input of Pb and Pb-210 to Crystal Lake occurs by wet deposition. More than 80% of the Pb entering the lake appears to be derived from anthropogenic sources. This input of anthropogenic Pb has resulted in an eight-fold increase in sediment Pb concentrations from 19 to 145 μg/g over the past 150 years.

The net removal of Pb-210 from the water column occurred primarily as short-term deposition events. Deposition of Pb-210 was enhanced by elevated biological activity during bloom periods. Accelerated deposition of Pb-210 also was observed during fall turnover. The rate of deposition during these events exceeded the annual mean rate of 1.81 dpm/cm^2/yr by two to three-fold. Over the whole year the rate of Pb-210 deosition varied by as much as an order of magnitude.

Deposition of Pb-210 was most rapid during the productive stratified period averaging 2.09 dpm/cm^2/yr. Consequently, the residence time of Pb-210 was 0.1 yr or less. The rate of Pb-210 deposition decreased 33% to 1.4 dpm/cm^2/yr during the less productive unstratified period. Over this period the residence time of Pb-210 averaged several tenths of a year. The overall mean residence time of Pb-210 is 0.2 yr, the same as that estimated for stable Pb.

At least 90% of the standing crop of Po-210 in Crystal Lake is formed *in situ* by decay of atmospherically supplied Pb-210. The activity ratio Po-210/Pb-210 averaged 0.66 in the whole lake during the stratified period. The subequilibrium condition of Po-210 relative to Pb-210 is attributed to: 1. the preferential removal of Pb-210 by plankton, and 2. the rapid

removal of Pb-210 from the water column. Over this period Po-210 exhibited a mean residence time of 0.7 yr. The residence time of Po-210 averaged several years during the unstratified period. The overall mean residence time of Po-210 is 2.6 yr. This suggests that it is recycled approximately 13 more times than Pb-210 before being removed from the water column. As a result of extensive recycling a large portion of the Po-210 decays to stable Pb-206 in the water column and never reaches the sediment.

Based on the Pb-210 geochronology of four sediment cores, the mass sedimentation rate in Crystal Lake is about 8 mg/cm^2/yr (0.14 cm/yr). Using this estimate of the sedimentation rate and the vertical distributions of Pb and Pb-210 in the sediment, the present day (1979) fluxes are 1.2 μg/cm^2/yr and 1.75 dpm/cm^2/yr, respectively. Of the total Pb flux at least 1.0 μg/cm^2/yr can probably be ascribed to accumulation of anthropogenic Pb and the majority of it appears to be delivered by atmospheric fallout.

The dynamics of lead transport from the atmosphere to the lake surface and through the water column have been studied in a manner such that observations of spatial and temporal variability include seasonal effects. The non-steady-state input and removal processes necessitate this type of approach if a realistic description of geochemical regimes in lakes is to be developed.

TABLE OF CONTENTS

Foreword..

Abstract.. iii

Figures... iv

Tables.. viii

Acknowledgments... x

.... xii

1. Introduction...
2. Conclusions.. 1
3. Background... 3
    - Introduction.. 5
    - Lead in the Atmosphere.................................... 5
    - Lead-210 and Po-210 in the Atmosphere..................... 5
    - Additional Sources of Pb-210 to Lake Waters............... 7
    - Distribution of Pb-210 and Po-210 in the Water Column..... 10
    - Estimation of Particulate Fluxes.......................... 11
4. Objectives... 15
5. Study Site... 19
    - Introduction.. 21
    - Description of Study Lake................................. 21
    - Atmospheric Monitoring Site............................... 21
6. Sampling Methodology and Analysis............................ 23
    - Atmospheric Sampling...................................... 24
    - Crystal Lake Sampling..................................... 24
    - Preparation of Samples for Analysis....................... 25
    - Instrumental Analysis..................................... 28
7. Analytical Data.. 33
    - Aerosol Measurements...................................... 35
    - Rainfall Measurements..................................... 35
    - Crystal Lake Temperature Profiles......................... 40
    - Crystal Lake Suspended Particulate Profiles............... 42
    - Presentation of Water Column Data......................... 44
    - Distribution of Pb-210.................................... 46
    - Distribution of Po-210.................................... 57
    - Distribution of Rn-222 and Ra-226......................... 58
    - Concentration of Pb in Crystal Lake....................... 60
    - Plankton Data... 64
    - Results of the Sediment Trap Experiments.................. 64
8. Estimates of Atmospheric Deposition.......................... 67
    - Introduction.. 70
    - Wet Deposition.. 70
    - Dry Deposition: The Modeling Approach..................... 70

74

Estimates of Total Atmospheric Fluxes.................... 86
9. Dynamics of Pb-210 in the Water Column.................... 87
Development of the Two-Layer Model.................... 87
Description of the Two-Layer Model.................... 91
Results of the Two-Layer Model.................... 94
Possible Sources of Pb-210 to Crystal Lake.................... 105
Summary of Results.................... 107
10. Dynamics of Po-210 in the Water Column.................... 108
Introduction.................... 108
Po-210/Pb-210 Disequilibrium in the Water Column.................... 108
Summary.................... 114
11. A Closer Examination of Particulate Phase Transport.................... 115
Introduction.................... 115
Fractionation of Pb and Pb-210.................... 115
Fractionation of Pb-210 and Po-210.................... 116
An Evaluation of In-Lake Flux Estimates.................... 119
12. Sediment Geochronologies of Pb and Pb-210.................... 122
Introduction.................... 122
Pb-210 Geochronology.................... 122
Stable Pb Geochronology.................... 125
Sediment Distributions of Al and C.................... 127

References.................... 130

Appendices

A. Radioactive Growth and Decay Calculations.................... 144
B. Atmospheric Data.................... 148
C. Crystal Lake Data.................... 154

LIST OF FIGURES

Number		Page
1	Uranium-238 decay series	9
2	Morphometry of Crystal Lake	22
3	Sampling locations in Crystal Lake	26
4	Atmospheric concentrations near ground level as a function of time	36
5	Average atmospheric concentrations as a function of impactor stage	38
6	Concentrations of Pb and Pb-210 in rainfall as a function of time	41
7	Temperature profiles for Crystal Lake	43
8	Suspended particulate matter profiles for Crystal Lake	45
9	Vertical profiles of Pb-210 and Po-210 in Crystal Lake on 5 June 1979	47
10	Vertical profiles of Pb-210 and Po-210 in Crystal Lake on 23 June 1979	48
11	Vertical profiles of Pb-210 and Po-210 in Crystal Lake on 11 July 1979	49
12	Vertical profiles of Pb-210 and Po-210 in Crystal Lake on 16 August 1979	50
13	Vertical profiles of Pb-210 and Po-210 in Crystal Lake on 1 September 1979	51
14	Vertical profiles of Pb-210 and Po-210 in Crystal Lake on 22 September 1979	52
15	Vertical profiles of Pb-210 and Po-210 in Crystal Lake on 13 October 1979	53

Number Page

16 Vertical profiles of Pb-210 and Po-210 in Crystal Lake on 27 October 1979.. 54

17 Vertical profiles of Pb-210 and Po-210 in Crystal Lake on 10 May 1980.. 55

18 Vertical profiles of Pb-210 and Po-210 in Crystal Lake on 7 June 1980.. 56

19 Summary of Po-210/Pb-210 disequilibria in Crystal Lake for all sampling dates.. 59

20 Frequency distributions of Po-210:Pb-210 activity ratios in Crystal Lake for all sampling dates.......................... 61

21 Average vertical profiles of Ra-226 and Rn-222 in Crystal Lake... 63

22 Predicted deposition velocities at z = 5 m as a function of particle diameter for U* = 25 cm/sec and selected value of z_0.. 78

23 Predicted deposition velocities at z = 5 m as a function of particle diameter for U* = 55 cm/sec and selected values of z_0.. 79

24 Average atmospheric concentrations during the warm season as a function of particle diameter............................. 80

25 Average atmospheric concentrations during the cold season as a function of particle diameter............................. 81

26 Representation of the two-layer model used to examine transport dynamics of Pb-210 in Crystal Lake.................. 92

27 Mean total activity ratios Po-210:Pb-210 and inventories of dissolved and particulate phase Po-210 and Pb-210 in Crystal Lake as a function of time.................................. 118

28 Vertical distributions of Pb and unsupported Pb-210 in Crystal Lake sediments....................................... 124

29 Vertical distributions of Al and C in Crystal Lake sediments... 128

LIST OF TABLES

Number | | Page
1 Average Metal Concentrations as a Function of Particle Size.... 37

2 Average Elemental Concentrations as a Function of Particle Size.. 39

3 Average Elemental and Isotopic Ratios as a Function of Particle Size.. 40

4 Summary of Po-210/Pb-210 Activity Ratios in Crystal Lake....... 60

5 Weighted Mean Metal Concentrations and Po-210:Pb-210 Activity Ratios in Plankton.. 65

6 Estimated Fluxes from Sediment Trap Experiments................ 68

7 Comparison of Mean Fluxes in Crystal Lake During Stratified and Unstratified Periods...................................... 69

8 Wet Deposition Estimates...................................... 71

9 Washout Factors and Specific Activities....................... 73

10 Average Dry Deposition Estimates.............................. 83

11 Atmospheric Deposition Estimated from Snow Cores.............. 85

12 Estimates of Total Atmospheric Fluxes......................... 86

13 Whole Lake Integrated Pb-210 Profiles......................... 88

14 Dissolved and Particulate Phase Standing Crops of Pb-210 in Crystal Lake.. 89

15 Results of the Two-Layer Model for Pb-210 Using an Average Per-Interval Atmospheric Input................................ 95

16 Results of the Two-Layer Model for Pb-210 Using an Average Dry Deposition and a Varible Wet Deposition.................. 96

Number Page

17 Comparison of Atmospheric Input and Particulate Phase Removal from the Water Column During the Stratified Period..... 97
18 Comparison of Estimates for the Paramters I, T, S, and S'...... 98
19 Suspended Particulate Matter Standing Crops.................. 99
20 Residence Times of Dissolved and Particulate Phase Pb-210 in Crystal Lake Estimated from the Two-Layer Model............... 104
21 Mean Residence Times of Dissolved and Particulate Phase Pb-210 in Crystal Lake for the Stratified and Unstratified Periods.... 105
22 Whole Lake Integrated Po-210 Profiles......................... 108
23 Dissolved and Particulate Phase Standing Crops of Po-210 in Crystal Lake.. 110
24 Mean Activity Ratios Po-210/Pb-210 and Residence Times of Po-210 in Crystal Lake.. 111
25 Fractionation of Pb-210/Po-210 and Pb-210/Pb Among Various Phases Transporting Metals in Crystal Lake.................... 115
26 Evaluation of Trapping Efficiencies.......................... 120
27 Sedimentation Data for Crystal Lake Cores..................... 123
B-1 Rain Data.. 149
B-2 Aerosol Data... 150
B-3 Size Differentiated Aerosol Data............................ 151
C-1 Temperature Profiles....................................... 155
C-2 Profile Data for SPM, pH, Pb-210, and Po-210.................. 156
C-3 Plankton Data.. 159
C-4 Sediment Trap Data.. 160
C-5 Sediment Trap Data: Elemental and Isotopic Ratios............ 161
C-6 Summary of Pb-210 Sediment Analyses and Associated Experimental Data.. 162
C-7 Summary of Al and Pb Sediment Analyses....................... 163

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SECTION 1

INTRODUCTION

Natural levels of Pb in the earth's crust average about 13 μg/g. Recent measurements of Pb concentrations in the atmosphere, lakes and oceans, and glaciers indicate that natural reservoirs and fluxes of Pb in the biosphere have been completely overwhelmed by extensive mining and dispersal of industrial Pb. Consequently, the average concentration of Pb in the biosphere has been elevated by an estimated factor of >20 over neolithic levels (Patterson et al. 1976a). The surface waters of the North Pacific, for example, are believed to contain about 10 times more Pb now than in prehistoric time (Schaule and Patterson 1979).

The earth's atmosphere has received widespread contamination by anthropogenic Pb since about 4500 yr before present (Patterson 1971). Industrial Pb has polluted all parts of the earth's troposphere by a minimum factor of 100 (Elias et al. 1975). Evidence suggests that considerable quantities of Pb and other trace metals reach lakes and oceans through the atmosphere (Robbins and Edgington 1975, Duce et al. 1976). Very little is known, however, concerning the mechanisms of deposition of Pb into lakes and oceans from the atmosphere. The efficiency and the parameters controlling removal of atmospheric Pb to surface waters by wet and dry fallout remain major unanswered questions.

There are two reasons for studying the Pb cycle in natural systems: 1. To determine the extent of Pb contamination and 2. to determine the mechanisms and controls on its distribution. It is, therefore, important to know the extent of Pb pollution in various facets of the environment and the manner in which the pollution was transferred. The potential health hazard to humans from extensive Pb pollution has been demonstrated by Nriagu (1978).

The dynamics of the cycling regime of Pb in the atmosphere and hydrosphere are largely unknown, despite extensive measurement of Pb concentrations in the environment. Considerable uncertainty in the reliability of many of these measurements has frustrated attempts to model various aspects of delivery and subsequent behavior of Pb in lakes and oceans. As pointed out by Brewer (1975) and Patterson et al. (1976b), even the concentration of Pb in seawater is not known with any degree of certainty. The same can be said of freshwater systems.

The present lack of direct information on Pb concentration and speciation in natural waters seriously limits the understanding of its transport in lakes. Consequently, detailed theoretical analyses of Pb solution equilibria have been tried as an approach to circumvent this problem. The varied chemical composition of lakes however makes it impossible to generalize about Pb speciation (Chow 1978). The presence of dissolved and particulate organic matter further complicates the investigation of Pb in the aquatic environment. Indeed, the calculated theoretical concentrations of Pb--as well as many other trace metals--in seawater and freshwater are orders of magnitude higher than the best currently measured values (Turekian 1977). Seawater actually contains the smallest concentration of Pb yet measured in any natural substance on earth--0.001 to 0.005 ng/g (Schaule and Patterson 1979).

If information regarding the spatial concentration of Pb in lakes is conspicuously deficient, less information is available describing the details of temporal or seasonal variations. To further compound the problem, models to describe the variation of Pb concentration with time and depth in a lake may need to include factors to account for variability of source loading, morphometric considerations, climatological effects, and sediment-water interactions. Recycling of Pb in the lake must be considered when estimating input and removal rates. The removal rate and permanency of such removal depend on internal chemical, physical, and biological factors. Interactions with animate and inanimate particles may, in some situations, be the most important variable controlling Pb concentration in the water column (Patterson et al. 1976b).

The extent and nature of sediment-water interactions may be important to the in-lake cycling of Pb. This may be particularly important during the period of thermal stratification when the typically oxygen-deficient hypolimnion is in contact with a large pool of sediment Pb. The sediments also contain the record of Pb deposition in the lake. By correctly reading and interpreting this preserved geochronological record, the history of Pb input to the lake can be reconstructed.

This investigation examined the correspondence between atmospheric loading, internal cycling, and sediment accumulation of Pb in a small oligotrophic lake located in a semi-remote area of northern Wisconsin. The approach was to use Pb-210 as a natural tracer for atmospheric stable Pb supplied to the lake. The high precision and accuracy capabilities of Pb-210 measurements relative to comparatively large stable Pb analysis uncertainties allow some of the important interactions responsible for maintaining the Pb inventories to be ascertained and the resultant fluxes between them identified. From this information a more complete picture of the Pb cycle in natural waters may be formed.

SECTION 2

CONCLUSIONS

This research examined some of the aspects of the geochemical cycles of Pb, Pb-210, and Po-210 by following their transport from the atmosphere through Crystal Lake. It has been shown that non-steady-state processes greatly influence atmospheric input and in-lake removal of these metals. Input and removal processes in the system as a whole, however, appear to approximate steady-state conditions over a time span of about 1 yr.

The mean atmospheric fluxes of Pb and Pb-210 for 1978 to 1980 were estimated to be 1.0 μg/cm^2/yr and 1.79 dpm/cm^2/yr, respectively. These fluxes may be considered representative of the year-to-year mean fluxes with the caveat that an uncertainty of about 20% is associated with each value. The atmospheric flux of Po-210 appears to be <1.0 dpm/cm^2/yr, or <10% that of Pb-210. Wet deposition accounts for at least 85% of the annual mean fallout of Pb, Pb-210, and Po-210 at this site.

Biological, chemical, and physical in-lake processes interact in a complex manner which subsequently determines the fate of Pb, Pb-210, and Po-210 in Crystal Lake. Their net removal from the geochemical regime(s) occurs primarily as short-term deposition events. Despite a scant biological population, the biota in Crystal Lake strongly influence transport dynamics of Pb-210 and Po-210. Plankton, in fact, appear to overwhelmingly mediate removal of Pb-210 and Po-210 from the water column during the productive stratified period. Fall turnover also is important in removing Pb-210.

The in-lake rate of Pb-210 deposition varied more than six-fold over the whole year. Deposition of Pb-210 during the statified period was estimated to be 2.09 ± 0.57 dpm/cm^2/yr. The flux was 33% less during the unstratified period (1.40 ± 0.48 dpm/cm^2/yr) than it was over the statified period. The annual mean in-lake flux of Pb-210 was estimated to be 1.81 ± 0.50 dpm/cm^2/yr. The excellent agreement between estimates of in-lake deposition and atmospheric supply of Pb-210 provides strong support for the contention that the atmosphere is the principal source of Pb-210 to Crystal Lake.

The mean residence times of Pb-210 in the dissolved and the particulate phases fluctuated by more than an order of magnitude (~ 0.01 to 1 yr). The surface mixed layer (SML) is more dynamic than the deep layer (DL) in this regard, especially during the productive stratified period. The overall mean residence times of Pb and Pb-210 in Crystal Lake essentially are equal at 0.20 yr.

Most of the Po-210 in Crystal Lake is formed *in situ* by decay of atmospherically supplied Pb-210. Extensive recycling, most likely biologically mediated, keeps Po-210 in the water column an average of 13 times longer than Pb-210. The residence time of Po-210 in the dissolved and the particulate phase is of the order of years. Thus, a large fraction of the Po-210 is lost in the water column by decay to stable Pb-206.

During the stratified period the residence time of Po-210 averaged 0.7 yr. The activity ratio Po-210:Pb-210 was 0.66 during the same period. This deficit of Po-210 relative to Pb-210 is attributed to preferential uptake and rapid deposition of Po-210 by biological pathways. When the lake was least productive, activities of Po-210 approached equilibrium levels with Pb-210.

The mass sedimentation rate in Crystal Lake appears to be about 8 $mg/cm^2/yr$ (0.14 cm/yr). Based on this estimate and the vertical distributions of Pb and Pb-210 in the sediment, the present day (1979) fluxes are 1.2 $\mu g/cm^2/yr$ and 1.75 $dpm/cm^2/yr$, respectively. Of the total Pb flux, 1.0 $\mu g/cm^2/yr$ can probably can be ascribed to accumulation of anthropogenic Pb. The input of anthropogenic Pb apparently has increased sediment Pb concentrations by eight-fold over the past 150 yr, from 19 to 145 μg/g.

This research has applicability to many lakes. Although the biological, chemical, and physical characteristics of Crystal Lake may be somewhat less complicated when compared to other lakes, metal cycling in the water column is probably controlled by analogous processes in the majority of lake systems. The removal of metals from surface waters of Lake Michigan, for example, may follow similar dynamics as observed in the whole water column of Crystal Lake.

It follows that most of the net deposition of metals in lakes is associated with biological, chemical, or physical in-lake events. It is recommended that future studies of geochemical regimes in lakes be designed to examine some of the aspects of the transport dynamics. Such studies should be coupled with an in-depth look at specific particle-metal associations. The role of plankton in metal transport also needs to be explored explicitly using *in situ* experiments. Detailed information on the specific phases carrying metals and on the corresponding transport kinetics is necessary for ultimately constructing a realistic picture of metal transport in lakes. The results of the present research indicate that within certain limitations the natural tracer Pb-210 is a valuable tool for obtaining direct and accurate experimental data on the geochemical regimes of metals in lakes.

SECTION 3

BACKGROUND

INTRODUCTION

This section presents a brief synopsis of various aspects of the geochemical cycles of stable Pb, Pb-210 and Po-210 in the atmosphere and hydrosphere. Discussion of the dynamics of Pb-210 cycling in the aquatic environment is devoted almost exclusively to marine systems. There appears to be no reliable data base for freshwater systems which describes the geochemistry of stable Pb, Pb-210, and Po-210 in the water column. Although the specifics of these processes probably differ between marine and freshwater systems, the basic mechanisms controlling the geochemical regimes are probably analogous. One aspect of this research investigated such a hypothesis.

LEAD IN THE ATMOSPHERE

Lead in the atmosphere originates from natural and anthropogenic sources. The release of Pb from natural sources is small (1.9×10^{10} g) compared to worldwide dissemination of anthropogenic Pb (44×10^{10} g) (Nriagu 1978). The spatial and temporal variation of Pb emission makes it difficult to estimate relative contributions of various sources to the annual flux of Pb into the atmosphere. Robinson and Robbins (1971) concluded that automotive Pb constitutes about 66% of the Pb released annually to the atmosphere. Chow and Johnstone (1965), Chow and Earl (1970), Chow (1970) and the National Academy of Sciences (1972) feel that >90% of the Pb in the atmosphere is from burning leaded gasoline. It is universally agreed that leaded gasoline has been the principal source of atmospheric Pb since about 1920.

To determine the origin of Pb aerosol a criterion called an "enrichment factor" (EF) has been used to broadly distinguish natural from anthropogenic Pb. The enrichment factor was defined (Rahn 1976) as:

$$EF = (Pb/M\ air)/(Pb/M\ crust) \quad (1)$$

where:

M is a reference element such as Al or Ca.

An enrichment factor close to unity suggests a crustal or natural source. A high enrichment factor (10^2 to 10^4) indicates anthropogenic origin. The enrichment factor has proven useful for distinguishing Pb origin at sites away from land areas, such as in the marine troposphere or polar regions. Caution must be used when interpreting the enrichment factor since the Pb:Al ratio of aerosol is generally inversely proportional to particle size (Colovos et al. 1974).

The average concentration of Pb in urban air ranges from 0.5 to 10 $\mu g/m^3$. The average for rural localities is 0.1 to 1.0 $\mu g/m^3$, while remote areas average <0.1 $\mu g/m^3$ (Nriagu 1978). The percentage of Pb in aerosol, like Pb concentration in the atmosphere, decreases from urban to remote sites. In most cases, where atmospheric Pb concentrations exceed 1.0 $\mu g/m^3$, Pb constitutes 1.0 to 10% of the aerosol. The percentage of Pb in aerosol drops to 0.1 to 1.0% in rural areas and declines to <0.1% in remote areas. The lowest present day average Pb concentration reported in the continental United States is 8.0 ng/m^3 (1.2 to 29 range) at White Mountain (3800 m elevation), California (Chow et al. 1972). Patterson (1965) estimates that the natural Pb concentration of the pristine atmosphere was probably about 0.6 ng/m^3.

Attention now is being focused not only on the atmospheric concentration of Pb, but also on its particle size distribution in the atmosphere. Information on the size distribution of atmospheric Pb can be important in identifying sources and sinks of aerosol Pb. Particle size data for aerosols is a major factor in most dry deposition models. Invariably, particle size and Pb concentration correlate in a manner which indicates that most of the Pb mass is submicron (<1 μm). As much as 33% of the Pb mass may be contained in supermicron (<0.1 μm) particles (Davidson 1977). A comprehensive survey of the atmosphere in 59 urban areas of the United States showed 25% of the total suspended Pb to have diameters of <0.16 μm and 75% to be <0.4 μm (Robinson and Ludwig 1967). The mass median equivalent diameter for aerosol Pb is about 0.5 μm (Lee et al. 1972). Janssens and Dams (1975) found this to be true for Pb at urban and remote continental sites.

Rain and snow remove aerosol Pb from the atmosphere with varying efficiencies. Lazrus et al. (1970) reported that the average concentration of Pb in rain over the continental United States is about 34 μg/kg. (We feel that 20 μg/kg is a more reasonable, up-to-date estimate.) Several studies (Cawse 1974, ACRES Report 1975) have indicated that the Pb concentration of precipitation is usually highest in winter. Experimental evidence indicates that snowfall has a greater removal efficiency for Pb from the atmosphere than rain. Although the concentration of Pb in snow has not been measured extensively, it appears to be slightly higher than the concentration of Pb in rain at a given locality. Scavenging and washout of aerosol by precipitation are complex processes (Gatz and Dingle 1971) and the precise mechanisms of aerosol removal from the atmosphere are unknown.

In addition to rain and airborne concentrations of Pb, deposition rates of Pb have been measured. The least is known, however, about deposition of submicron particles where impaction and diffusional processes are primarily responsible for transferring them to the earth's surface. Deposition of atmospheric Pb varies spatially and temporally from location to location. Variations of atmospheric Pb deposition are caused primarily by changes in source intensity and meteorological conditions which affect atmospheric dispersion and mixing processes. Stolzenburg (1979) found that Pb concentrations in the Menomonee River Airshed (Wisconsin) fluctuate by at least one order of magnitude. Lead deposition in the continental United States varies from 0.1 μg/cm^2/yr in isolated areas of the California mountains to >40 μg/cm^2/yr in large cities. The average deposition rate of Pb in the United States is about 1 μg/cm^2/yr (Nriagu 1978).

Wet and dry deposition of aerosol Pb is of comparable importance in some situations. Cawse (1974) found the average ratio of dry to total deposition of Pb at rural locations in the United Kingdom to be about 52%. An extreme case was reported by Peirson et al. (1973). They estimated dry deposition of Pb at Lake Windermere to be <5% of the total Pb deposition. It is obviously difficult to estimate the removal efficiency of Pb by wet and dry processes. The predominance of wet or dry deposition at a given locality is governed by a variety of variables, particularly specific meteorological factors.

The chemical composition of aerosol Pb is not well known. Ter Haar and Bayard (1971) determined the composition of Pb in aerosols from a rural site to be 30% $PbCO_3$, 28% $(PbO)_2$, and 21% PbO. The remaining minor Pb compounds were composed of various sulfates, bromides, chlorides, and bromochlorides. Biggins and Harrison (1979), however, found the major Pb compound in ambient aerosol to be PbSO4 . $(NH_4)_2SO_4$. Laxen and Harrison (1977) observed various Pb compounds in roadside runoff. The forms of Pb included $PbCO_3$, $Pb(HCO_3)^+$, and organic complexed Pb. Apparently, some conversion or decomposition of Pb compounds occurs on the aerosol since Hirschler et al. (1957) and Ter Haar and Bayard (1971) have determined that automobile Pb is exhausted primarily as PbBrCl. In summary, Pb is found in aerosol in a variety of inorganic forms as well as unidentifiable organic Pb compounds.

The types of Pb compounds residing in atmospheric particulates indicate that these compounds may be soluble to some degree in water. Cawse (1974) found that 50 to 90% of airborne Pb in particles collected from rural areas of the United Kingdom was soluble in water. A large fraction of radiolead in atmospheric particulates was found to be leachable (Koide et al. 1975). Hodge et al. (1978) observed that 40 to 50% of aerosol stable Pb and Pb-210 was soluble in seawater. These studies suggest that aerosol Pb may influence the concentration of Pb in surface waters of lakes.

LEAD-210 AND POLONIUM-210 IN THE ATMOSPHERE

Unsupported Pb-210 originates primarily in the atmosphere due to a remarkable feature of the uranium-238 decay series. In the decay scheme Rn-222, a noble gas, emanates from the earth's surface to the atmosphere at an average rate of 0.70 to 0.75 atom/cm^2/sec (Wilkening et al. 1975). Decay of Rn-222 ($t_{1/2}$ = 3.83 days) proceeds in the atmosphere by a series of short-lived involatile daughter radionuclides to Pb-210 ($t_{1/2}$ = 22.26 yr). The decay scheme is depicted in Figure 1.

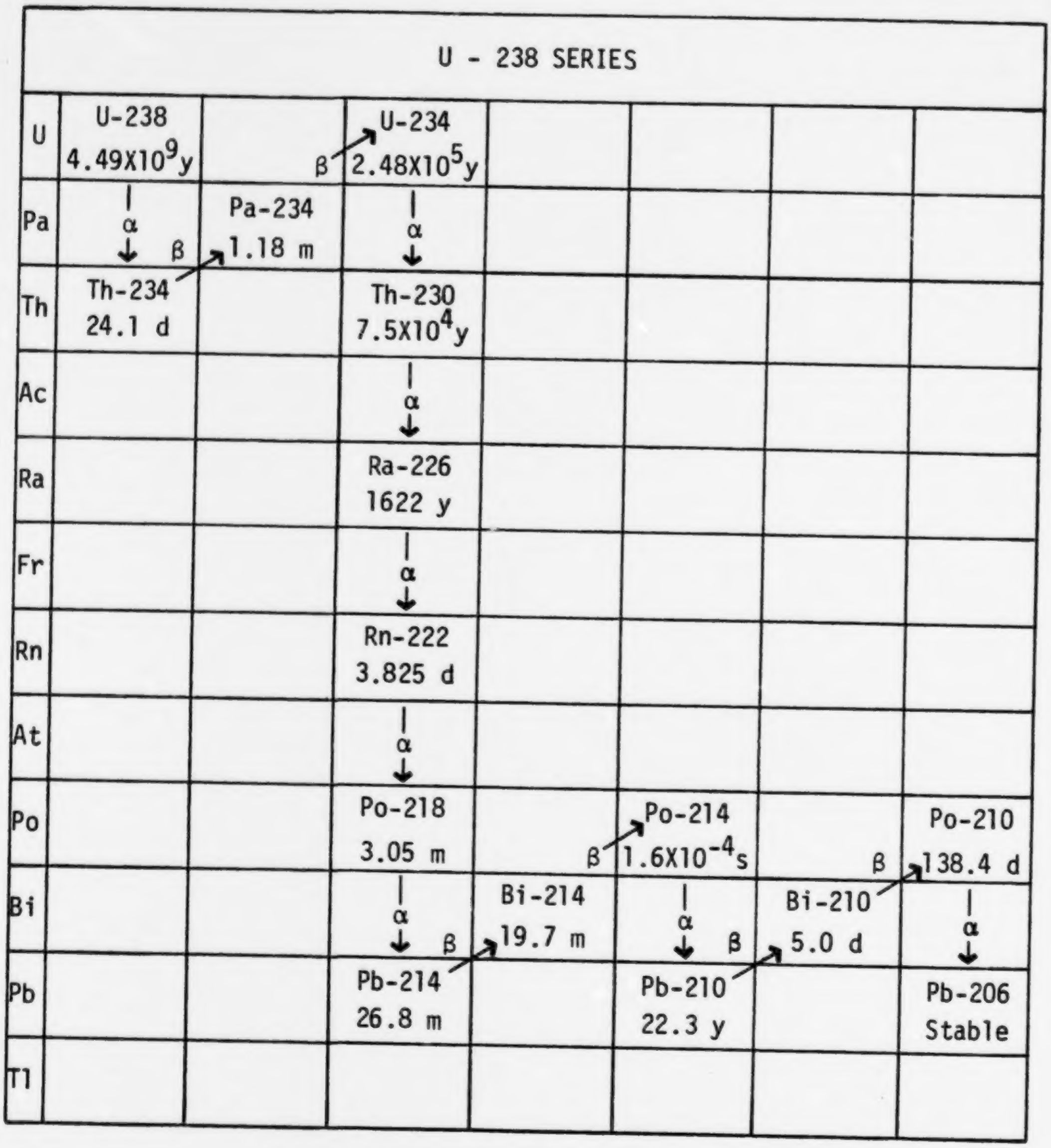
The daughter radionuclides produced from Rn-222 decay are chemically reactive and become associated with aerosol particles (Nozaki and Tsunogai 1973, Turekian et al. 1977). The decay half-lives of the intervening nuclides are short relative to the mean residence time of tropospheric aerosol so that almost all atoms emitted as Rn-222 are redeposited as Pb-210. Removal of Pb-210 from the troposphere to the earth's surface by wet and dry deposition occurs on a time scale of a few days to several weeks (Poet et al. 1972, Moore et al. 1973). Direct atmospheric deposition is the principal source of unsupported Pb-210 to the oceans (Bacon et al. 1976) and many freshwater lakes (Koide et al. 1972, Robbins and Edgington 1975).

Some of the Po-210 ($t_{1/2}$ = 138.4 days) in the atmosphere is supported by decay of Pb-210. The amount of Po-210 produced in the atmosphere from decay of Pb-210 is approximately 10% of the total tropospheric Po-210 (Moore et al. 1976). This means a large majority of tropospheric Po-210 must be unsupported. Moore et al. (1976) estimated that 60% of the Po-210 in clear air over the United States is derived from entrainment of soil dust. Unsupported Po-210 contributed by dust storms, coal burning, forest fires, and plant exudates accounts for the remaining excess Po-210 in the troposphere (Mattson 1970, Moore et al. 1976). The flux of Po-210 to the earth's surface is only about 10% that of Pb-210 (Poet et al. 1972). The majority of the Po-210 in seawater is formed by decay of Pb-210 *in situ* (Bacon 1975).

The concentration of Pb-210 in the atmosphere has been measured at several locations worldwide. Atmospheric concentrations of Pb-210 generally vary from 1 to 50 dpm.$10^3/m^3$. Since significant Rn-222 exhalation occurs only from land areas of the earth, the Rn flux to the atmosphere varies as a function of latitude. The Pb-210 concentration in the troposphere follows the same spatial trend as Rn-222 and reaches maximum concentration at about 50°N.

Atmospheric concentrations of Pb-210 are about 20 dpm.$10^3/m^3$ at Boulder, Colorado (Poet et al. 1972). Hodge et al. (1978) measured Pb-210 concentrations in air over Ensenada, Mexico, and La Jolla, California. The aerosol Pb-210 averaged 20 dpm.$10^3/m^3$ at Ensenada and 50 dpm.$10^3/m^3$ at La Jolla. An average of 40 dpm.$10^3/m^3$ can be calculated for air over the continental United States (Rangarajan et al. 1976).

Measurements of atmospheric Po-210 are sparse, but concentrations usually average an order of magnitude lower than corresponding Pb-210 concentrations. Moore et al. (1973) reported that Po-210 concentrations over the west central United States average 0.5 dmp.$10^3/m^3$ under clear air conditions. They found that aerosol Po-210 usually was in the range 0.2 to 2 dpm.$10^3/m^3$. These findings agree with those of an earlier study by Poet et al. (1972), who found Po-210 concentrations between 0.1 and 7 dpm.$10^3/m^3$ at Boulder, Colorado.



U - 238 SERIES

U	U-238 $4.49X10^9y$	β ↗	U-234 $2.48X10^5y$				
Pa	α ↓ β ↗	Pa-234 1.18 m	α ↓				
Th	Th-234 24.1 d		Th-230 $7.5X10^4y$				
Ac			α ↓				
Ra			Ra-226 1622 y				
Fr			α ↓				
Rn			Rn-222 3.825 d				
At			α ↓				
Po			Po-218 3.05 m	β ↗	Po-214 $1.6X10^{-4}s$	β ↗	Po-210 138.4 d
Bi			α ↓ β ↗	Bi-214 19.7 m	α ↓ β ↗	Bi-210 5.0 d	α ↓
Pb			Pb-214 26.8 m		Pb-210 22.3 y		Pb-206 Stable
Tl							

Figure 1. Uranium-238 decay series.

Francis et al. (1970) measured Po-210 in rainfall at Madison, Wisconsin. They found concentrations of 0.4 to 7 dpm/liter. At Boulder, Colorado, Poet et al. (1972) found that Po-210 concentrations in rainfall were between 0.3 and 1 dpm/liter. Lead-210 concentrations in the same rainfall were higher, generally between 7 and 17 dpm/liter. Highly variable concentrations of Pb-210 in rainfall (1.7 to 24.8 dpm/liter) also were observed at Fayetteville, Arkansas by Gavini et al. (1974).

The atmospheric flux of Pb-210 to the earth's surface has been estimated from measurements of Pb-210 in air, rain, lake sediment, and soil. Turekian et al. (1977) have summarized these estimates on a worldwide basis. Moore and Poet (1976) estimated an annual mean flux of 1.6 dpm/cm^2/yr for the central United States on the basis of the Pb-210 profile in a soil horizon from Colorado. Fisenne (1967) calculated a rate of 1.2 dpm/cm^2/yr from measurements of Pb-210 in a soil profile collected in Maryland. Extensive measurement of Pb-210 in rain and dry fallout at New Haven, Connecticut was conducted by Benninger (1976). The results indicate a Pb-210 flux in the eastern United States of 0.92 ± 0.09 dpm/cm^2/yr. Robbins and Edgington (1975) have estimated the Pb-210 flux to Lake Michigan from measurements of Pb-210 in sediments. Their data indicate the Pb-210 flux to Lake Michigan is 0.31 to 1.44 dpm/cm^2/yr. For locations in the continental United States, the Pb-210 flux appears to be 1 to 2 dpm/cm^2/yr.

ADDITIONAL SOURCES OF Pb-210 TO LAKE WATERS

In addition to atmospheric deposition, Pb-210 and Po-210 may be supplied to lake waters by soil erosion, riverine transport, or groundwater seepage. By comparing Pb-210 activity profiles of various soil horizons with the measured atmospheric flux of Pb-210, Benninger et al. (1975) determined that soils are essentially 100% efficient in retaining Pb-210 supplied to them, i.e., no measurable loss of Pb-210 was found from the soil horizon other than by radioactive decay. The sequestering of Pb-210 by soil materials appears to be most effective for soils with a high organic matter content (Benninger et al. 1975, Lewis 1977). Lewis (1977) calculated that 0.05%/yr of the soil standing crop of Pb-210 is lost under normal weathering and erosion conditions from the soil terrain of the Susquehanna River headwaters. This estimate agrees with that of Benninger et al. (1975) for the lower portion of the Susquehanna River system (0.02%/yr). Servant and Delapart (1979) estimate that the soil retains at least 87% of the atmospheric Pb-210 supplied to the watershed of the Ariege, Garome, and Hers Rivers in southwestern France. Thus, it may be concluded from these studies that Pb-210 has low mobility in a soil system where soil particles and organic matter exhibit strong sequestering properties. For more impervious types of terrain, however, more of the Pb-210 deposited may be lost through surface runoff. The high retention efficiencies found by Benninger et al. (1975) and Lewis (1977) cannot always be expected.

Several investigations of Pb-210 transport by rivers and groundwater have demonstrated the low mobility of dissolved Pb-210. Rama et al. (1961) studied the transport of Pb-210 by the Colorado River system. The source waters contained large amounts of dissolved Pb-210 mobilized by uranium mining operations. It was found that the downstream dissolved Pb-210 concentration (dpm/liter) decreased to about 2% of the source water average concentration. Scavenging of Pb-210 by suspended particles was suggested as the removal mechanism. Benninger et al. (1975) and Lewis (1977) found <0.01 dpm/liter Pb-210 in headwaters of the Susquehanna River. No measurable dissolved Pb-210 was present further downstream at the river mouth.

Lead-210 in groundwater is derived primarily from decay of dissolved Ra-226 which is leached from surrounding rocks. Holtzman (1964) conducted a survey of groundwater Pb-210 in Illinois. He found that the Pb-210 concentration (0.4 dpm/liter) was always less than the Ra-226 concentration (10 dpm/liter). The ratio Pb-210:Ra-226 averaged 4×10^{-3} in groundwater. The Pb-210 activity also was generally 2% of the 20 dpm/liter value expected from direct infiltration of rainwater. Lewis (1977) found Pb-210 activities between 0.007 and 1.12 dpm/liter in groundwater feeding the Susquehanna River. However, headwater streams containing recently discharged groundwater averaged only 0.01 dpm/liter of Pb-210. These studies indicate rapid removal of dissolved Pb-210 from groundwater through scavenging and precipitation, resulting in low levels (<1 dpm/liter) being supplied to streams and lakes.

DISTRIBUTION OF Pb-210 AND Po-210 IN THE WATER COLUMN

Information on the distribution and concentration of Pb-210 in lakes is meager. No measurements of Po-210 have been reported for lake waters. Krishnaswany et al. (1971) determined that the average concentration of Pb-210 in Lake Tansa (India) was 0.2 dpm/liter. The data indicate that the atmosphere is the principal source of Pb-210 to Lake Tansa and no significant Pb-210 is derived from the drainage area.

Schell (1974) measured the stable Pb and Pb-210 in Lake Washington. The mean concentration of Pb-210 in surface water was 0.041 dpm/liter. A residence time in Lake Washington of about 80 days was estimated for stable Pb and Pb-210 using a one-dimensional box model. Schell (1974) concluded from his study that stable Pb and Pb-210 in Lake Washington originate primarily from atmospheric loading.

The majority of investigations of the Pb-210 and Po-210 distribution in the water column have been concerned with marine systems. The logistics of separating dissolved and particulate phases in large volumes of seawater hampered the initial studies of Po-210/Pb-210 disequlibria in the water column. Since dissolved and particulate phases were usually not distinguished, data interpretation was limited to general statements concerning the total Pb-210 and Po-210 distribution in seawater. Some of the important observations which prompted future studies are now presented.

Rama et al. (1961) were the first to measure Pb-210 concentrations in seawater. They found that the atmospheric supply of unsupported Pb-210 to the sea surface was much greater than the amount of Pb-210 produced *in situ* from Ra-226 decay. The Pb-210 activity of the mixed layer was less than in deeper water despite the atmospheric input of Pb-210. It was suggested that Pb-210 must be removed rapidly from surface seawater to depth by biological or physical (i.e., sedimentation) processes. Their results prompted other investigators to study the processes affecting the Pb-210 distribution in greater detail.

Bruland et al. (1974a) measured Ra-226 and Pb-210 concentrations in unfiltered North Pacific seawater. In waters of low productivity Pb-210:Ra-226 activity ratios were typically >1.0. This suggested that the supply rate of unsupported Pb-210 by atmospheric deposition exceeded the rate of removal of Pb-210 from surface seawater to depth. In contrast to unproductive waters, Pb-210:Ra-226 activity ratios in highly productive waters were 0.1 to 0.3. The subequilibrium concentrations of Pb-210 relative to Ra-226 led them to suggest that activities of the biosphere rapidly removed Pb-210 from the mixed layer. The removal rate in this case exceeded the flux of unsupported Pb-210 from the atmosphere.

Levels of Pb-210 and Po-210 in marine plankton were measured previously. Cherry (1964) and Shannon and Cherry (1967) reported unsupported Po-210 in marine plankton at levels of 4.7 pCi/g for zooplankton and 2.8 pCi/g for phytoplankton (dry weight). Unsupported Pb-210 and Po-210 also were detected in biological materials collected from the Atlantic and Pacific Oceans by Beasley et al. (1969). Shannon et al. (1970) measured Pb-210 and Po-210 in seawater and marine plankton collected off the coast of Africa. It was found that Po-210 activity accounted for most of the α-activity in zooplankton and a smaller fraction in phytoplankton. Concentration factors of Pb-210 and Po-210 from seawater to wet zooplankton were 870 and 20,000, respectively. For phytoplankton the concentration factors were 890 for Pb-210 and 5400 for Po-210. More importantly, they observed the atom ratio Pb-210:Po-210 removed from the mixed layer was of the same magnitude as the measured atom ratios (Pb-210:Po-210) in zooplankton and phytoplankton. This observation indicated that Pb-210 and Po-210 may be transported from the mixed layer to depth primarily by plankton. Residence times of these nuclides in the mixed layer, based on removal of plankton, were calculated to be about 5 yr for Pb-210 and 0.6 yr for Po-210.

Cherry et al. (1975) conducted a more detailed study of the role of marine plankton in the cycling of Po-210 in the mixed layer. A residence time due to zooplankton metabolic activity was calculated as 0.9 yr for Po-210. This calculation prompted the suggestion that zooplankton metabolic activity--fecal pellet removal in particular--is an important mechanism for removing Po-210 from surface seawater to depth.

Thomson and Turekian (1976) measured total Pb-210 and Po-210 activities in two ocean profiles collected from the Peru Basin. The purpose of the study was to evaluate the influence of suspended particulates in the water column on the distribution of Pb-210 and Po-210. The profile closest to the coast--where biological productivity was high--showed depletion of Pb-210 relative to Ra-226 at all depths. Marked excursions from radioactive equilibrium occurred in surface and bottom waters. Polonium-210 was deficient relative to Pb-210 at depth as well. In the profile collected from less productive waters, the Ra-226, Pb-210, and Po-210 activities were close to equilibrium values at all depths. Thomson and Turekian (1976) concluded that scavening and removal of Pb-210 by particulate matter (biotic and abiotic) in areas of low productivity were not as efficient as in highly productive waters. It was suggested that a range of residence times in the water column, dependent on water column characteristics, may be anticipated for Pb-210 and Po-210. The data reported by other investigators (Bruland et al. 1974a) supports this conclusion.

On the basis of the Pb-210 concentration in plankton and biological productivity estimates, Nozaki and Tsunogai (1976) demonstrated that it was impossible to provide a major Pb-210 flux from the mixed layer of the Pacific to depth by the settling of planktonic debris alone. Benninger (1976) later showed the same thing for Atlantic coastal waters. Kharkar et al. (1976) came to the same conclusion while studying Pb-210 and Po-210 in Caribbean waters. It was determined that the actual flux of particles carrying Pb-210 and Po-210 to depth unidirectionally could not have the Po-210:Pb-210 activity ratios of bulk zooplankton. The results indicate Po-210 is concentrated by plankton and rapidly released to solution. In that sense Po-210 behaves like nutrient elements.

In summary, settling of particulate matter appears to be a major process removing Pb-210 and Po-210 from the mixed layer (Bruland et al. 1974a, Thomson and Turekian 1976, Nozaki et al. 1976, Nozaki and Tsunogai 1976). The particles carrying Pb-210 and Po-210 to deep water are most likely highly processed debris of biogenic origin (Kharkar et al. 1976). This hypothesis seems reasonable, since most observed particulate matter is of biological origin within the surface layer of the ocean (Bishop et al. 1977). Furthermore, Craig et al. (1973) showed removal of Pb-210 produced in deep water by *in situ* Rn-222 decay probably resulted from adsorption by settling particulate matter.

Nozaki and Tsunogai (1976) estimated that the residence time of Pb-210 varies from approximately 1 yr in surface seawater to 100 yr in deep water. In contrast, Po-210 appears to have a residence time of 0.6 yr in surface seawater and only 2 yr at depth (Thomson and Turekian 1976). To gain a better understanding of the processes controlling the distribution of Pb-210 and Po-210 in the ocean, extensive sampling of surface and deep waters was conducted by a few investigators during the GEOSECS program. A brief summary of the results follows.

The most recent investigations of Pb-210 and Po-210 in seawater distinguished dissolved and particulate phases. Somayajulu and Craig (1976) measured dissolved and particulate Pb-210 activities at two stations in the South Atlantic. Particulate phase Pb-210 varied from 0.3% of the total Pb-210 in surface seawater to 15% in deeper water. The particulate phase Pb-210 activity increased by a factor of 40 from surface to bottom but still only comprised 10% of the total Pb-210 activity in the water column. By comparing particulate Pb-210 activities with suspended particle concentrations measured by Brewer et al. (1976), Somayajulu and Craig (1976) showed that the increase in particulate Pb-210 activity with depth was due to the increase in absolute activity of the particulate phase rather than an increase in the mass of suspended particles. These data support scavenging of dissolved Pb-210 in the water column and indicate that particles do not become saturated with Pb-210 as they settle.

Bacon et al. (1976) measured Pb-210 and Po-210 in dissolved and particulate fractions for sampling stations located in the tropical and eastern North Atlantic and the Pacific Ocean. Within the mixed layer nearly all of the data indicate a deficiency of dissolved Po-210 relative to Pb-210. Using a material balance for the mixed layer it was estimated that Po-210 was removed from solution with a residence time in the dissolved phase of 0.6 and 0.11 yr in the particulate phase. This indicates that Po-210 is removed efficiently from the mixed layer by sinking particles.

More than 90% of the Pb-210 in surface seawater resides in the dissolved phase (Bacon 1977). Lead-210 was found to have a longer residence time than Po-210 in the dissolved phase, about 2.5 yr. Bacon et al. (1976) assumed particulate Pb-210 was removed at the same rate as particulate Po-210 (i.e., 0.11 yr) as suggested earlier by Turekian et al. (1974). Polonium-210 concentrations, however, have been shown to be strongly influenced by biological activity in the water column. The effect seems to be less pronounced for Pb-210, which implies that Pb-210 is not incorporated into particulate matter as efficiently as Po-210. Thus, Po-210 may be rapidly removed from highly productive surface waters by fecal pellet deposition, whereas, Pb-210 may be removed primarily by adsorption on sinking particulate matter. Consequently, the removal rate of Pb-210 from surface waters would be limited by the adsorption process. Craig et al. (1973) suggested that this also may be the case for Pb-210 in the deep ocean.

Bacon et al. (1976) estimated that >50% of the Po-210 removed from the mixed layer is recycled in the thermocline region. Analogous calculations for Pb-210 suggested <5% is recycled. Even though Po-210 was found to be more reactive than Pb-210 in the water column, total inventories of Pb-210 and Po-210 over the entire water column showed no significant departure from secular equilibrium.

Schell (1977), working independently of the GEOSECS program, observed differences in speciation of Pb-210 between open ocean and coastal waters. Of the total Pb-210, >90% was in the dissolved phase at all open ocean sampling sites in the Pacific. Coastal regions near Washington state, however, had >75% of the total Pb-210 associated with the particulate fraction. Residence times of particulate Pb-210 was estimated to be on the order of days in nearshore waters and 2 to 3 yr in open ocean waters. Benninger (1976) obtained similar removal rates for particulate Pb-210 in coastal waters of Long Island Sound.

The different residence times of Pb-210 in the two oceanic zones apparently reflect its distribution in the water column. The data reported by Thomson and Turekian (1976), Somayajulu and Craig (1976), and Schell (1977) indicate the distribution of Pb-210 in seawater is--at least in part--a function of the suspended particulate concentration. These data also support the proposition (Turekian 1977) that, "The major sequestering of trace metals in the oceans is mediated through sinking particles."

In conclusion, very little quantitative information regarding supply, transport, and removal of Pb-210 and Po-210 in the ocean was obtained from investigations that did not attempt to partition total Pb-210 or Po-210 into soluble and particulate states. It is evident from the most recent studies of Pb-210 and Po-210 in seawater that total Pb-210 and Po-210 concentrations should be separated into dissolved and particulate phases to obtain the most useful data for interpreting their distribution in the water column. The kinetics of some of the processes influencing the distribution of Pb-210 and Po-210, and presumably other trace metals, can then be examined in greater detail.

ESTIMATION OF PARTICULATE FLUXES

Deposition of suspended particulate matter occurs due to the inefficiency of recylcing mechanisms operating in the water column. Most particles in the water column have biogenic origin in the surface water (Bishop et al. 1977). The vertical flux of a substance depends on the size distribution, density, and settling behavior of the particles conveying the material to the sediments (Bishop et al. 1977). Investigation of suspended particulates in the ocean suggests that their size distribution may be described as an exponential function with median sizes of 2 to 8 μm (Gordon 1970, Sheldon et al. 1972, Honjo 1978). The total concentration of particulate matter and the form of the size spectra vary seasonally, especially in productive waters (Menzel and Ryther 1960, Sheldon et al. 1972).

Rare, larger (>20 μm) particles dominate the particle flux in the ocean (McCave 1975). Aggregation of smaller particles, largely due to biological recycling, is thought to be the norm in the surface ocean. Non-aggregated particles appear to form a background haze whose distribution is controlled primarily by horizontal advection (McCave 1975). The larger particles composing the settling flux are thus most important in transporting chemical elements to the sediments (Gardner 1977, Brewer et al. 1980). The chemical composition of these large particles is of primary interest in estimating the apparent mass fluxes of various elements.

Buat-Menard and Chesselet (1979) estimated the large particle flux of selected major and minor elements in the tropical North Atlantic. They based their calculated elemental fluxes on the average flux of particulate organic C leaving the mixed surfce layer and the element:C ratio in large biogenic particles. The large particle elemental flux was shown to be particularly important for transmitting Pb and other trace metals to depth.

Investigation of suspended particulate matter in the water column has been used to study various aspects of the biogeochemical cycle of selected elements (Bishop et al. 1977). The chemical composition of suspended particles has been determined by collection of water samples, filtration, and subsequent elemental analysis (Brewer et al. 1976, Krishnaswami and

Sarin 1976, Bishop et al. 1977, Shafer 1981). These procedures offer an inferior estimate of flux since settling velocities of the different size fractions are unknown and estimates based on isotopic data or Stokes law calculations contain model assumptions (Spencer et al. 1978).

Sediment Traps

Sediment traps offer a method of directly measuring the downward movement of materials with the limitation that turbulent effects can cause such devices to undertrap or overtrap sinking particles (Gardner 1977, Hargrave and Burns 1979). Hence, an estimate of material deposition from the water column or accumulation of materials in sediments is possible. Mineralogic, elemental, and isotopic data for trapped material, in addition to the mass flux, permit detailed analysis of the interaction of particles with the water column. This provides important information on particulate material during its passage through the water column, especially if the vertical chemical flux can be determined as a function of depth.

Sediment traps furnish an experimentally determined flux through a depth interval integrated over the time frame of the experiment. The settling rate (or suite of rates) of the particles is, of course, not explicitly determined. The settling rate can be inferred, however, from the measured radionuclide distribution in the water column. Krishnaswami et al. (1976), Spencer et al. (1978), and Brewer et al. (1980) have discussed the application of a scavenging, settling model from which mean settling rates of the particles can be estimated using radioisotope data. Such a model was originally proposed by Craig et al. (1973) to describe Pb-210/Ra-226 disequilibria in the deep ocean.

Spencer et al. (1978) have discussed several problems inherent in sediment trap experiments. One of the most troubling problems is that trapping efficiency tends to be biased toward the large particle size fraction. Trapping efficiency must be estimated. Brewer et al. (1980) have demonstrated that trapping efficiency for particles can be based on radionuclide flux transcending the water column. Data for Pb-210, Th-230, Th-228, and Th-234 was used to supply estimates of particle trapping efficiencies.

Another problem plaguing sediment trap experiments is a significant contribution to the measured primary flux by resuspended bottom sediments. Spencer et al. (1978) estimated the relative amounts of primary and resuspended fluxes at sites in the Sargasso Sea by assuming that the primary flux of aluminosilicate material was attributable to atmospheric deposition. The elemental fluxes of trapped material were normalized to the estimated atmospheric flux of Al to provide a first-order estimate of primary fluxes.

It is evident that results of sediment trap experiments must be interpreted cautiously. Important questions relating to the construction of the sedimentary record by nascent material in the water column remain to be answered. Direct observation of the particulate flux through sediment trap experiments offers a unique opportunity to study particle-water column interactions.

Sediments

The mean rate of deposition of particulate matter and its chemical composition are recorded in the sediments. Numerous investigators have examined recent and historical sediments to identify anthropogenic inputs of metals associated with industrialization (Bruland et al. 1974b, Goldberg et al. 1978, Bertine and Mendeck 1978). Sediment accumulation rates may be estimated for various chemical elements by determining the vertical distribution of an element in the sediment and the mass sedimentation rate. Mass sedimentation rates in lakes have been deduced from time stratigraphic markers preserved in the sediment. The radionuclides Pb-210 and Cs-137 are valuable geochronological tools of contemporary geochemists. These techniques have been used to estimate mass sedimentation rates in the Great Lakes (Bruland et al. 1975, Edgington and Robbins 1976, Robbins et al. 1978), in several smaller lakes (Krishnaswami et al. 1971, Koide et al. 1973, Schell 1974) and in coastal marine environments (Koide et al. 1972, 1973, Bruland 1974, Smith and Walton 1980).

The Pb-210 dating scheme was first introduced by Goldberg (1963), who applied the technique to glacier ice packs. The use of Pb-210 as a geochemical tracer stems from its incorporation in sediments primarily as atmospherically supplied unsupported Pb-210. The depth-time profile of Pb-210 in undisturbed sediment should be in accord with its radioactive half-life. Bruland (1974) and Robbins (1978) have discussed the application of Pb-210 to lacustrine and coastal marine sediments. Supporting geochronological information is sometimes obtained from analysis of Cs-137 activities and fossil pollen assemblages (Robbins and Edgington 1975, Robbins et al. 1978).

In many instances sediment reworking as a result of biological activity or depositional and erosional processes associated with wave action or storm surges have distorted or obscured the sedimentary record. Excellent examples of the latter can be found in Edgington and Robbins (1976) and Smith and Walton (1980). The interpretation of sedimentation regimes in biologically disturbed sediments is difficult. This type of post-depositional process is apparently common in Great Lakes sediments (Robbins and Edgington 1975, Robbins et al. 1977). Total disruption of the sedimentological record usually occurs and results in a completely mixed interval 4 to 6 cm below the sediment-water interface. Guinasso and Schink (1975) and Robbins et al. (1977) have calculated biological mixing rates for sediments where mixing by benthic fauna has been invoked.

When the vertical distribution of stable Pb and Pb-210 in the sediments is known, it is possible to examine the historical input of Pb to the lake (Petit 1974, Schell 1974, Robbins and Edgington 1975, Oldfield et al. 1980). Shirahata et al. (1980) measured Pb-206:Pb-207 ratios in Pb-210 dated sediment profiles of a subalpine pond located in the High Sierras. It was shown that Pb in the sediments is derived solely from atmospheric deposition of anthropogenic Pb. The sediment Pb concentration was estimated to have increased four-fold during the 1720 to 1976 interval. The major part of the Pb contamination has occurred in the last 130 yr (1845 to present). Elevated concentrations of Pb are found commonly in surface sediments of the Great Lakes (Robbins and Edgington 1975), numerous small lakes (Schell 1974, Peterson 1973), and coastal marine sediments (Bertine and Mendeck 1978, Christensen et al. 1978, Goldberg et al. 1978). The Pb pollution histories of the different sedimentary environments suggest that anthropogenic Pb input greatly exceeds natural Pb input to these systems.

By examining the sediment to determine historical input of Pb (and other metals) to the lake, it is possible to estimate present day deposition of Pb in the system. Although this method of estimating flux of Pb yields only a time-averaged input over several years, it should generally agree with those estimates based on water column information. Thus, in a system where atmospheric input exceeds all other source inputs, atmospheric supply, water column transport, and sediment accumulation should be coupled. This research attempted to examine some of the correspondence between these metal compartments.

SECTION 4

OBJECTIVES

Principal routes for transport of Pb to many lakes include wet and dry deposition of aerosols. If Pb contributed by local sources to a lake constitutes only a minor portion of the total Pb budget, then removal of Pb from the water column should be coupled with its atmospheric supply. Furthermore, accumulation of Pb in the sediment should reflect the atmospheric input. The extent to which Pb is cycled and its residence time in the water column are definable in the ideal case.

Some of the important chemical, physical, and biological factors regulating the net fluxes and concentration of Pb in the lake can be identified if accurate mass balances are constructed linking sources and sinks. Once the magnitude and direction of the resultant fluxes are determined, correspondence between atmospheric supply, internal lake transport, and sediment-water column interactions can be evaluated with regard to spatial and temporal variation of Pb concentration in the lake. An idea of the patitioning of Pb between dissolved and particulate forms should provide some insight into the process regulating internal transport dynamics. To obtain an apparent true picture of net input and removal processes, the lake must be studied in a manner to include seasonal effects. The water temperature, for example, will affect sediment-water column exchange equilibria, organic matter decomposition rates, plankton growth rates, and lake mixing. Seasonal changes in atmospheric loading to the lake may significantly affect the inventory of Pb in the water column.

The primary objective of the research was to examine various aspects of supply and removal of Pb in an integrated lake system. The approach was to use Pb-210 as a natural tracer to provide experimental evidence concerning the origin and transport of stable Pb in a lake with very low Pb levels (i.e., the order of 200 ng/kg). Specific objectives were directed toward obtaining information about movement of Pb betwen various compartments linking the Pb cycle in natural waters. The specific objectives adopted were:

1. To estimate atmospheric deposition of stable Pb, Pb-210, and Po-210 to Crystal Lake.
2. To develop a general picture of the processes controlling the distribution of Pb-210 and Po-210 in oligotrophic lake waters by utilizing material mass balances.

3. To estimate removal of particulate phase Pb-210 from the water column and correlate the temporal variation in the estimated flux with in-lake processes.

4. To construct a rigorous material mass balance for Pb-210 in Crystal Lake using the atmospheric supply, its distribution and transport in the water column, and its accumulation in the sediments.

SECTION 5

STUDY SITE

INTRODUCTION

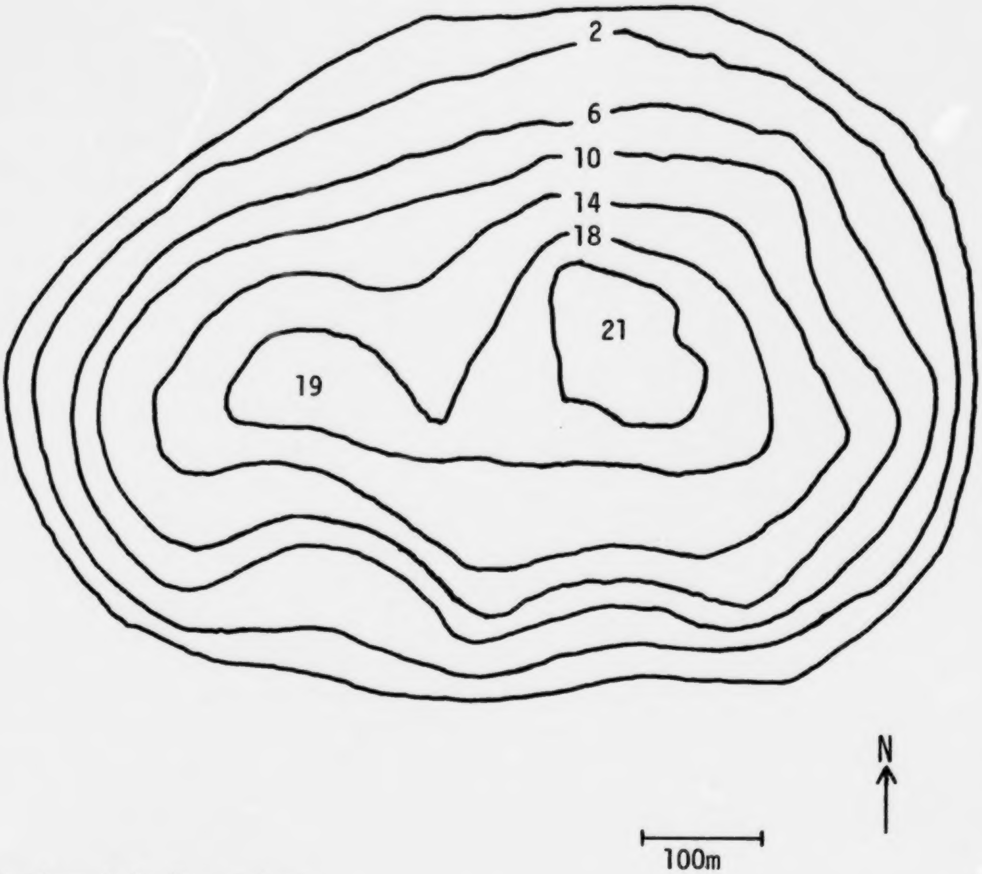
To study various aspects of supply, transport, and removal of atmospherically supplied Pb in a lake, a site was needed where the atmosphere would be the primary source of Pb-210 (and stable Pb). Essentially all other sources of Pb-210 would contribute insignificantly to the in-lake inventory. This condition was desirable so that a material mass balance model could provide a definitive picture of processes controlling the Pb regime in the lake. Also, confounding littoral effects should be at a minimum. One additional constraint on site selection was that the lake be thermally stratified during summer. This allowed cycling of Pb-210 in the lake to be compared during stratified and unstratified periods.

DESCRIPTION OF STUDY LAKE: 46°0.3' N, 89°36.9' W, elevation 500 m above MSL

Crystal Lake was chosen as the study lake. The lake is located in the Northern Highlands Lake District of north-central Wisconsin (Vilas County) and has several features which make it ideal. These features include: 1. No inflowing or outflowing streams, 2. an extremely small watershed, 3. minimal biological activity, and 4. little apparent groundwater inflow. In addition, motor boats are not allowed on the lake.

The morphometry of Crystal Lake is depicted in Figure 2. All morphometric information reported here is based on a map of the lake made in 1939 by the Wisconsin Conservation Department lake survey (Clarkson Map Co., Kaukauna, Wisconsin). The lake has a maximum depth of 21 m and a surface area of 3.1×10^5 m^2. During the summer stratified period of 1979 the mean epilimnetic depth was 7.5 m. The corresponding epilimnetic volume was estimated to be 1.7×10^6 m^3. The combined metalimnetic and hypolimnetic volume is 1.4×10^6 m^3.

Crystal Lake is an infertile seepage lake and is probably the most oligotrophic lake in Wisconsin. The lake occupies a sandy depression between two recessional moraines. Water seeps into the oval-shaped basin through outwash sands that contain little or no carbonates. Hence, the lake has slightly acidic soft water exhibiting high transparency (e.g., secchi disc transparency 8.5 to 10 m).



Morphometric Parameters:

Maximum Depth	21 m
Mean Depth	10 m
Surface Area	3.1 X 10^5 m^2
Volume	3.1 X 10^6 m^3
	1.7 X 10^6 m^3 Epilimnetic (0 – 8m) 1.4 X 10^6 m^3 Metalimnetic and Hypolimnetic (8 – 21m)

Figure 2. Morphometry of Crystal Lake (depth in m).

The biological and chemical charactersitics of Crystal Lake were first described by Birge and Juday (1929 1930). More recently Baker (1974) conducted a survey of the lake and concluded it has not changed biologically or chemically in the past 50 yr. Although the lake is thermally stratified from late June to early October, the hypolimnion usually remains oxygenated throughout this period, indicating minimal groundwater inflow. Also, it suggests that there is little oxidation of organic matter taking place in the hypolimnion. The pH of hypolimnetic water ranges between 5.5 (20 m) and 6.0 (10 m). In the epilimnion the pH varies from 6.0 to 6.5 (this study).

Crystal Lake is classified as an oligotrophic lake due to total P levels of <10 μg/liter. Despite silica concentrations of $\leq$ 30 μg/liter (Colman 1979), Black et al. (1963) identified more than 80 species of diatoms in the sediments. The low P and silica levels in Crystal Lake compared to those of nearby lakes indicate that little runoff from the surrounding area enters the lake (Colman 1979, Stauffer 1981). The surface soil around the lake is generally sandy and the lake receives diffuse surface runoff from only a few hectares of land. Due to low topographic relief around the lake and the permeable soils, runoff is probably minor. The entire area surrounding the lake (and shoreline) is heavily forested by pine trees. The lake is, therefore, well protected from wind, which allows it to become strongly (thermally) stratified when the air temperature is greater than the water temperature.

The sediments of Crystal Lake were characterized by Twenhofel and Broughton (1939). Quartz sands dominate in the littoral zone and to a depth of 8 to 10 m. Organic rich biogenic material (50% dry weight) composes the major part of the sediment in the deeper water zone. Diatoms and pollen grains constitute a major portion of these sediments (Black et al. 1963).

ATMOSPHERIC MONITORING SITE: 46°3.3' N, 89°39.2' W, elevation 500 m above MSL

Atmospheric sampling was conducted in an open field on the grounds of the Northern Highland Forestry Headquarters. This site is located on the east shore of Trout Lake approximately 6.4 km northwest of Crystal Lake. The atmospheric monitoring station consisted of two high volume air samplers and one rain sampler. A rain gauge was mounted on a post about 2 m from the rain sampler. A daily record of the high and low temperature, relative humidity, wind speed (10 m), wind direction, and rainfall (separate gauge) was available from a small Wisconsin Department of Natural Resources (WDNR) weather station adjacent to the sampling site.

SECTION 6

SAMPLING METHODOLOGY AND ANALYSIS

ATMOSPHERIC SAMPLING

Various sampling methodologies were used to collect samples for estimating the atmospheric loading of Pb, Pb-210 and Po-210 to Crystal Lake. Integrated aerosol and precipitation samples were collected bimonthly from June through October. Monthly samples were obtained from November through May.

Aerosol Sampling

Total suspended particulate (TSP) samples were collected with a General Metal Works high volume air sampler. A Sierra high volume cascade impactor was used to collect size-differentiated aerosol samples. Aerosol was collected on Whatman 41 filter paper media. Whatman 41 was chosen because it exhibits low blanks for metals such as Pb (Dams et al. 1972, Bate et al. 1976, Hirsbrunner and Wangersky 1975). Filter paper was transported to and from the sampling site sealed in polyethylene bags. After sample collection, 20 X 25-cm filters were folded in quarters and impactor slotted paper was folded in half so that the collection surface was inward.

Aerosol samples were collected continuously from June 1979 to June 1980. The TSP and size-fractionated aerosol were collected simultaneously by two samplers situated about 25 m apart. High volume air samplers were mounted on wooden platforms so that the air collection height was about 2 m above ground level. The mass flow of air was maintained constant at 1.1 m^3/min by means of mass flow controllers. Automatic timers were programmed to operate the air samplers on a predetermined schedule. The samplers were run every 2 or 3 days for 12 h. The 12-h collection interval extended from noon until midnight and then went from midnight to noon on the next sampling day. Generally, samples were collected over a 2-week period (72 to 84-h collections). This sampling schedule was felt to provide a relatively unbiased integrated aerosol sample which could be used to estimate dry deposition of stable Pb, Pb-210, and Po-210. The sampling period was lengthened during winter to insure collection of sufficient material for reliable mass (TSP) and elemental analyses.

Rain Sampling

Rain was collected by an automatic Wong rain sampler. The sampler was modified to minimize contamination of the sample by fugitive dust during dry periods (Stolzenburg 1979). In addition, the sampler was painted with metal-free paint. Rain was collected by a 25-cm diameter polyethylene funnel. The funnel was connected to a 5-liter polyethylene collection bottle with Teflon tubing (0.3 cm diameter). Small-diameter tubing was used to minimize evaporation of the sample during dry periods.

Rain sampling was conducted in 1979 from May to October. During May and October the sampler cover froze in the open position on several occasions. Samples collected during these months were discarded since it was felt the rain was probably contaminated by dry deposition and windblown debris. During warmer months--June to September--rain was collected continuously over 2-week periods. The integrated rain samples were used to estimate annual wet deposition of stable Pb, Pb-210, and Po-210.

Snow Sampling

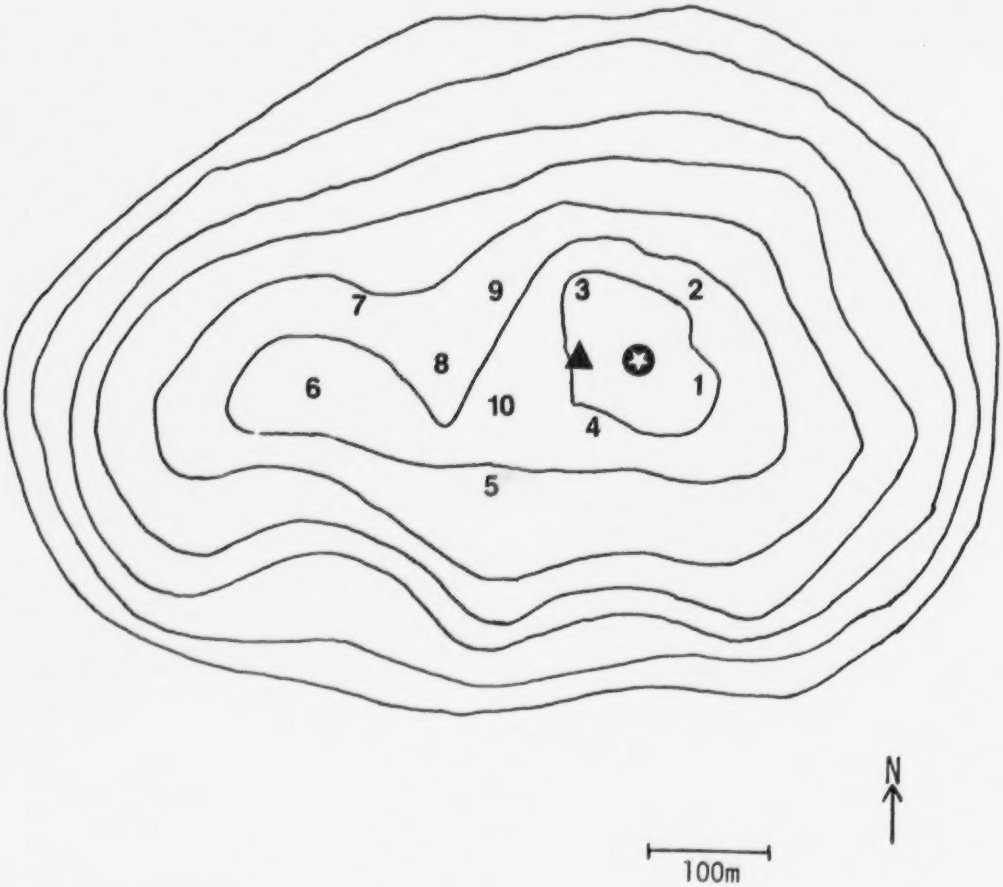
During the winter of 1979 to 1980 snow was collected on several occasions. Samples were obtained by placing a clean polyethylene sheet on the ground and later collecting 10-cm diameter cores of snow from atop the sheet. Snow collected in this manner was placed in large polyethylene bottles and allowed to melt at room temperature in the laboratory.

CRYSTAL LAKE SAMPLING

Sampling locations in Crystal Lake are annotated on a morphometry map of the lake shown in Figure 3. All sampling was done from an unpainted aluminum boat. The boat was rowed to the sampling location and anchored during sample collection. The temperature profile of the water column was obtained on each sampling date prior to sampling. A Whitney thermister-type probe with a resolution of about 0.2°C was used for all temperature measurements.

Water Sampling

Lake water was collected by lowering a weighted polyethylene tube (0.6 cm diameter) to the appropriate depth and drawing water into a sample bottle. The weight consisted of a tightly capped 1-liter polyethylene bottle filled with sand. The weight was suspended with nylon string 1 m below the end of the sampling tube. The on-board end of the sampling tube was connected to a polyethylene one-way valve and to a 20-liter glass carboy lined with a polyethylene bag. The carboy was evacuated such that by


7
9
3
2
8
6
10
1
4
5
N
100m

Sampling Notation:

✪ Water Sampling

▲ Sediment Trap Array

Numbers 1-10 Sediment Cores

Figure 3. Sampling locations in Crystal Lake.

opening the valve, lake water was drawn into the sample container. To minimize carry over contamination from one sampling depth to the next, several tube volumes were drawn into an extra carboy and the sampling tube was subsequently connected to the appropriate collection bottle.

Unfiltered surface water samples were collected from Crystal Lake for stable Pb analysis during October 1979. These water samples were collected in 1-liter TFE Teflon bottles cleaned according to Patterson and Settle (1976). The samples were collected with gloved hands from the bow of the boat while the boat was being rowed forward. The sample bottle was submerged about 25 cm below the water surface and the cap was removed to collect the sample. The bottle was capped at depth, brought into the boat, and sealed in two polyethylene bags. The samples were placed on ice and returned to Madison, Wisconsin.

Plankton Sampling

Plankton was collected by fishing a No. 25 mesh (64-μm aperature) nylon plankton net. The precautions outlined by Martin and Knauer (1973) were followed to avoid metal contamination during collection and analysis. Particulate matter caught by the net probably includes phytoplankton, zooplankton, and detritus. Microscopic examination of some plankton samples indicated they consisted primarily of phytoplankton and zooplankton.

Sediment trap Collections

Sediment traps were used as a method of estimating apparent mass and elemental downward fluxes in Crystal Lake. Traps were constructed according to the recommendations of Gardner (1977). Cylindrical traps were used in this work and had an aspect ratio of ~ 3:1 (30 X 10 cm). According to Gardner (1977), material collected by traps of the above design should closely represent actual fluxes in current conditions of ≤ 9 cm/sec. Currents in the hypolimnion of Crystal Lake are about 1 to 2 cm/sec (Colman 1979).

Traps were constructed of PVC pipe with plexiglass bottoms. A polyethylene fitting was attached to the bottom of the trap to allow material to be washed out of the trap directly into a sample bottle. An array of three traps was suspended from a submerged float using a polypropylene line. The entire apparatus was anchored firmly by a 13.6 kg weight buried in the bottom sediment. One trap was deployed in the metalimnion, another in the center of the hypolimnion, and the third just above the bottom sediment. The top of the traps were estimated to be 10.5, 5.5, and 2 m above the sediment-water interface. Material was collected during three sampling intervals: 1. Summer stratified period, 2. fall period of weak stratification during which the hypolimnion was heated by downward mixing of warm surface water, and 3. fall turnover period.

Sediment Coring

Sediment cores were collected from the deep hole area of Crystal Lake with a Jenkins corer. The water depth was estimated to be 17 m at all coring locations. Coring could not be conducted in shallower areas of the lake due to the abundant growth of the moss *Drepanocladus aduncus* var. *aquaticus* on the bottom (Juday and Birge 1932). Four apparently undisturbed 30-cm cores (~ 35 cm^2) were collected on 31 July 1979. The integrity of the cores was checked by visual examination immediately after collection. The sediment appeared to be homogeneous and there was no indication of layering. The surface sediment was evidently collected intact since chironomid burrow tubes projected about 1 cm above the sediment-water interface.

Cores were kept at approximately *in situ* temperature (4 to 5°C) during transport to the Trout Lake Laboratory. The cores were carefully sectioned using cleaned polyethylene apparatus to avoid metal contamination. The uppermost portion of the cores (>3 cm) was sectioned in 0.5-cm intervals. The rest of the core was sectioned in either 1 or 2-cm intervals. Extruded sections of the core were placed in polyethylene bags and stored at 4°C.

PREPARATION OF SAMPLES FOR ANALYSIS

Cleaning of Labware, Reagents, and Sampling Apparatus

Doubly distilled deionized water from a pyrex still was used in preliminary rinsing and acid soaking. Water for final rinsing and sample preparation was obtained from a sub-boiling point quartz still (cleanest water).

Ammonium pyrrolidinedithiocarbamate (APDC) was purified by extraction using purified CCl_4. Reagent grade CCl_4 was purified by extraction with 2 *N* HCl.

New Teflon, polyethylene, and quartz ware was washed with acetone to remove greasy dirt. The labware was subjected to soaking for at least 5 days in 50% HNO_3 (Teflon and quartz) or 50% HCl (polyethylene). Final acid soaking was in dilute HNO_3 (0.05%) and dilute HCl (0.05%) for at least 3 days for each acid. Patterson and Settle (1976) have found that dilute acid is very efective in leaching Pb from surfaces. After acid cleaning, Teflon and quartz ware were rinsed with the cleanest water and stored in polyethylene bags. Polyethylene sample bottles were filled with the cleanest water and soaked until use.

Polyethylene bags were cleaned by shaking with a small amount of concentrated HNO_3. The bags were rinsed and partially filled with 0.1% HCl and soaked for 2 days. During the soaking period the bags were laid on their sides and turned over after the first 24 h. This allowed both sides of the bag to be cleaned with a small volume of acid. Cleanest water was used to rinse the bags after acid cleaning.

Polyethylene tubing for water sampling and sediment coring tubes were cleaned initially using 1% HCl. Thereafter, the polyethylene tubing was cleaned between sampling trips by soaking with 0.05% HCl for 3 days and rinsing with the cleanest water.

Sampling gear and samples were transported to and from Crystal Lake sealed in polyethylene bags. Non-talced polyethylene gloves were worn whenever labware or samples were handled.

Aerosol Samples

The TSP concentrations were determined by weighing filters before and after collection of aerosols. Since Whatman 41 is extremely hygroscopic, filters were weighed in a specially designed chamber where temperature (25 ± 2°C) and relative humidity (50 ± 1%) could be controlled (Strand et al. 1979). The chamber was located at the University of Wisconsin's Biotron Research Facility.

Approximately 20% of each 20 X 25-cm filter was sufficient to provide measurable quantities of Al, Pb, Pb-210, and Po-210. Subsamples were obtained by scoring the quartered filters with a stainless steel die and cutting out the inscribed area with stainless steel scissors. About 90% of each slotted impactor filter was required for reliable analysis of the previously mentioned elements. Stainless steel scissors were used to cut out nine impaction surfaces from the slotted filters.

Aerosol samples were digested using a modified version of the vapor phase technique originally described by Feldman (1977). Details of the technique for aerosol digestion were outlined by Stolzenburg (1979). To redissolve the digested residue HCl was used instead of HNO_3. The final HCl concentration was $\sim 2N$. Each sample was spiked with 1 to 1.5 dpm Po-208 to monitor recoveries of Po-210. The NBS coal fly ash (SRM 1633) and NBS Urban Particulate Matter (SRM 1648) were digested to check recoveries of Al and stable Pb. Recoveries of Al and stable Pb were within limits reported by NBS (Ondov et al. 1975, Stolzenburg 1979, and Gladney 1980).

Rain Samples

Rain was weighed in the collection bottle to estimate volume. Enough HCl was added to bring the pH near 1. At that time 25 ml was transferred to another container and held for stable Pb analysis. The remaining rain was spiked with ~ 1 dpm Po-208 and ~ 1 mg stable Pb. Concentration of the Po-210 and Pb-210 in rain was accomplished by Co^{+2}-APDC co-precipitation followed by filtration onto a 47-mm Millipore filter (0.45 μ) (Boyle and Edmond 1975). The chelated particles and filter were decomposed in quartz beakers by a 3:2 mixture of HNO_3:70% $HClO_4$. Samples were dried using a plate temperatures of ~ 330°C. Finally samples were redissolved with HCl and a small amount of water. The final acid concentration was ~ 2*N*.

Lake Water Samples

The samples for stable Pb analysis were weighed and acidified with Ultrex HNO_3 to 0.1% by weight on a clean air bench. The samples were heated at 60°C for 5 days to bring particulate Pb into solution. Following dissolution the samples were transferred to 500 ml Teflon beakers and the volume was reduced to ~ 25 ml. The water was evaporated on a clean air bench using an infrared heat lamp. Samples were weighed to determine the concentration factor obtained by reducing the volume. Lead analysis was performed by FAAS in the clean room facilities at the Department of Geology, University of Wisconsin-Madison.

Lake water for Pb-210 and Po-210 analysis was filtered at the Trout Lake Laboratory immediately after returning from sampling. The lake water was passed through 0.45-µm Millipore filters (142 mm) using a pressure filtration apparatus. Samples from the hypolimnion were handled first so they could be filtered as close to *in situ* temperature as possible. All water samples were filtered within 3 h of collection. Filtered water samples were weighed to the nearest 0.1 kg and the error in weight was estimated to be 0.8%.

A 1 to 2-liter subsample of the unfiltered water sample was pressure filtered through a 0.4-µm Nuclepore filter (47 mm) to estimate suspended particulate matter (SPM) concentrations. Proper handling and weighing procedures for estimating SPM concentrations were determined by Shafer (1980). All weighings were conducted in the clean room facilities.

Generally, three filters were used to filter a 15 to 20 kg aliquot of lake water. After filtration the filters were folded in half with the collection surface inward and stored in polyethylene bags. The filtrate was collected in a 20-liter polyethylene carboy. The volume was estimated and enough HCl was added (~ 4 ml/kg water) to bring the pH near 1. A few milligrams of stable Pb and 0.5 to 1.0 dpm Po-208 were added to monitor recoveries of Pb-210 and Po-210.

The filtrates were allowed to equilibrate with the yield tracers for 3 days before being concentrated by Co^{+2}-APDC chelate co-precipitation (Bacon 1975; Boyle and Edmond 1975). Samples were stirred slowly for 2 h to allow for nearly complete chelation of Pb-210 and Po-210. Yields were always $\geq$ 95%. The insoluble metal chelate was collected on a 0.45-µm Millipore filter.

Wet oxidation with HNO_3 and 70% $HClO_4$ was used to decompose the metal chelates. Particulate fractions were digested in the same manner. Digestions were performed in quartz beakers and the procedure was essentially the same as that for rain.

Sediment Trap Material

Material collected during the sediment trap study was filtered onto 0.45 µm Nucleopore filters (47 mm) using gentle suction. Weighings were conducted with a Perkin-Elmer microbalance under conditions outlined by Shafer (1981). A portion of the material was placed in quartz beakers, spiked with several dpm Po-208, and decomposed by the wet oxidation technique.

Sediment Samples

Bulk analysis of the sediment was performed to determine Al, stable Pb and Pb-210 distributions. A polyethylene syringe was used to transfer a measured volume of sediment from its storage bag to a polyethylene petri dish. Water was removed from the sediment by freeze drying. Samples were weighed before and after freeze drying so that porosity could be calculated. Subsamples of the dry sediment were used for density determinations as well as total and organic C analysis. To check for loss or contamination of stable Pb during the freeze-drying process, NBS River Sediment (SRM 1645) was slurried with water (%H_2O = 95%) and carried through the procedure. No measurable loss or contamination of Pb was found.

Approximately 1 to 2 g of dry sediment was digested with 5 ml HCl and 20 ml NHO_3. Digestions were performed in 100-ml round-bottomed quartz flasks. Several dpm Po-208 were added at the start of each digestion to monitor yields of Po-210. The sediemnt was boiled rigorously--for 24 to 36 h--until the solution turned pale yellow and the solid residue was white. At that time the samples were cooled and poured into polyethylene centrifuge tubes. A small amount of water was used to wash any remaining sediment from the flask into the tube. Samples were centrifuged for 45 min at 13,500 rpm to separate acid-resistant silicates from the nitric fraction. The nitric fraction was decanted from the tube into a quartz beaker. The beakers were placed on a hot plate and the volume was reduced using a plate temperature of ~ 150°C. When 2 to 3 ml were left, 2 ml of 70% $HClO_4$ were added. The plate temperature was increased to 300°C to dry the samples. Finally, 1 ml of HCl and a small amount of water were added to redissolve the residue. Samples were diluted to 25 ml and transferred to 30-ml polyethylene bottles.

The silicate residue was dissolved with 10 ml HF in a Teflon beaker (~ 100°C). When the volume of HF remaining was 2 to 3 ml, 70% $HClO_4$ was added and the samples were dried. The samples were redissolved with HCl as described previously.

The NBS River Sediment (SRM 1645) was digested in the same manner as Crystal Lake sediment. Measured recoveries of Al and Pb were within limits reported by NBS and Gladney (1980). The nitric fraction contained all the Pb. Consequently, Pb-210 determinations were performed only on the nitric fraction. Approximately 60 to 70% of the Al was contained in the nitric fraction. The HF (silicate) fraction contained the rest of the Al.

Polnium Plating Procedure

A calibrated Po-210 standard was used to work out the details of the plating and counting techniques. Samples were spiked with Po-208 to determine yields of Po-210 through the entire analytical procedure. Simultaneous counting of the Po-208 spike and Po-210 allowed the Po-210 recovery to be monitored easily. A stable Pb spike, free of Pb-210, was added to samples to monitor Pb-210 recoveries.

Separation of Po-210 for α-counting was performed by spontaneous deposition on Ag discs under conditions specified by Flynn (1968). The sample solution was ~ 2 HCl in all instances. Sediment samples were handled slightly differently than other samples. Hydroxylamine hydrochloride was added to the sediment sample solutions and heated in their sample bottles prior to plating (~ 1 h) to reduce Fe^{+3}.

All platings were conducted in 40-ml FEP Teflon beakers. Silver discs were coated on one side with a thin layer of Dow silicone grease and pressed firmly to the bottom of a Teflon beaker. The plating time was 4 to 6 h as recommended by Bacon (1975). Samples were processed as soon as possible after collection to preserve Po210-Pb210 activity differences, which decrease by a factor of 2 for every half-life of Po-210.

Following the initial separation of Po-210, samples were stored for 6 months to 1 yr to allow regeneration of Po-210 from Pb-210 decay. Determination of the newly produced Po-210 is a measure of the Pb-210 present in the sample. Using the two count rates of Po-210, the activities of Po-210 and Pb-210 at the time of sample collection can be calculated. Corrections are made for: Growth and decay between collection and analysis, analytical yields, reagent blanks, counting background, and counting efficiency. Details of the calculations and necessary assumptions are outlined in Appendix A.

Rn-222 and Ra-226 Procedure

Broecker (1965) described the basic handling and counting techniques which have become widely adopted for Rn-222. Key et al. (1979a) suggested method improvements to the convenience and precision of the Rn technique so that analytical variations can be distinguished more readily from environmental variations.

The analytical procedure described here is for Rn-222. The determination of Ra-226 is made by calculation from Rn-222 data and does not require a separate procedural discussion. Samples for Rn-222 and Ra-226 determination were collected in 20-liter glass carboys. The analytical technique consisted of removing Rn-222 from the lake water with He by bubble stripping. The He gas stream was passed through a scrubbing train to remove water vapor and CO_2. The Rn-222 was collected on a cold activated charcoal column. Subsequently, the Rn-222 was released by heating the column to

470°C and flushing into a [ZnS(Ag)] fluor-coated chamber for α-particle scintillation counting. A detailed description of the procedure, equipment, and calculations is given by Colman (1979).

INSTRUMENTAL ANALYSIS

Calibration of Pb-210 and Po-210 Activities

All of the analytical results reported for Pb-210 and Po-210 were calculated with reference to a calibrated Po-210 standard solution. The standard (#51007) was obtained from Isotope Products Laboratories, Burbank, California. Radiopurity of the standard was >99%. The activity of the standard was 0.109 μCi. The overall uncertainty in the calibration was 3.63% (99% confidence level). A primary standard was prepared by diluting the Po-210 solution (1.171 g, 2 HCl) by weight to a volume of ~ 100 ml with 2 HCl. A working standard (~ 10 ml) was prepared by diluting an aliquot of the primary standard. The working standard also was 2 HCl.

A solution of Po-208 tracer was obtained from the Environmental Measurements Laboratory, U.S. Department of Energy, New York. Calibration of this solution was performed periodically by mixing aliquots of Po-208 and Po-210 and determining the Po-208 activity. Over the course of this research no changes were observed in the activity of the Po solutions other than that attributed to radioactive decay.

Alpha Counting

Simultaneous activity measurements of Po-208 and Po-210 were performed by α-spectrometry using Si surface-barrier diode detectors (Princeton Gamma Tech). The detectors had an active surface area of 400 or 450 mm^2. Samples were counted in a vacuum chamber to give satisfactory resolution and minimize α-particle scattering. Following amplification, the detector signal passed through a multiplex router and was accumulated by a Tracor-Northern TN-1710 or RN-1706 pulse height analyzer. Sufficient resolution was usually achieved with the system to completely separate Po-208 (5.114 Mev) from Po-210 (5.305 Mev). Energy resolution, expressed as full peak width at half-maximum (FWHM), was estimated to be 40 to 50 Kev. Background count rates were <0.003 cpm and seldom exceeded 1% of the total sample activity. Sample counting times varied from <1 day to 7 days.

Counting Statistics

Counting error was determined from individual sample counts. The statistical counting error for the Po-208:Po-210 ratio was estimated as

$(1/N_{208} + 1/N_{210})^{1/2}$, where N_{208} and N_{210} designate the number of counts under each peak (Bacon 1975). The counting error for Pb-210 was calculated from the second count. Individual errors for the first and second counts were propagated to determine the counting error for Po-210.

AAS Analysis

A Perkin-Elmer 603 AAS was used for measurement of Al and stable Pb. Stable Pb was measured using an air-acetylene flame and a 4-inch single-slot burner. Analysis of rain and lake water for stable Pb was performed by FAAS using a HGA-2100 graphite furnace. Aluminum was measured using a 2-inch single-slot burner head and a nitrous oxide-acetylene flame. All AAS analysis was performed by means of a standard addition. Analytical precision was 3% for Pb analysis and 5% for Al. The Pb concentration of duplicate water samples was always within 5%.

Carbon Analysis

Total and organic C was measured using a LECO carbon analyzer. Total C was determined by diluting dry sediment with silica and weighing subsamples directly into the combustion crucible. Metallic Sn was added to facilitate oxidation of the sample. Organic C was determined after treating the sediment with 3% H_3PO_4 to remove inorganic C. Carbon standards were prepared from $CaCO_3$ and $Na_2C_2O_4$. Analytical precision, based on replicated sample analysis, was estimated to be 7%.

pH Measurements

All pH measurements were performed using a model 407A Orion pH meter equipped with a model 91-02-00 Orion combination electrode. The system was calibrated with two buffer solutions prior to each pH measurement. The overall uncertainty in the reported pH values (See Appendix A) was estimated to be approximately 0.1 pH unit.

SECTION 7

ANALYTICAL DATA

AEROSOL MEASUREMENTS

The aerosol concentrations of Pb, Pb-210, and Po-210 are shown in Figure 4 for June 1979 through June 1980. Activities of Pb-210 and Po-210 are corrected for growth or decay to the mid-point of the sampling interval. The weighted mean concentrations of Pb, Pb-210, and Po-210 were 21 ng/m^3, 22 dpm/dm^3, and 10 dpm/dm^3, respectively. During this 1-yr interval total suspended particlulate concentrations averaged 17 µg/m^3. (See Appendix A.)

Atmospheric Pb concentrations were lowest from January to May, averaging about 14 ng/m^3. Concentrations were higher during the summer, possibly because of increased automobile traffic. This area of northern Wisconsin is a popular summer tourist area.

The aerosol concentrations of Pb and Pb-210 generally followed the same trend. Lead-210 concentrations, however, tended not to vary as much as Pb concentrations. Hodge et al. (1978) observed that Pb and Pb-210 concentrations also followed similar trends in air over Ensenada, Mexico, and La Jolla, California. Most of the temporal variation of Pb and Pb-210 concentrations observed in this study probably were caused by changes in tropospheric mixing height. Stolzenburg (1979) has attributed large variations in atmospheric Pb concentrations over the Menomonee River Airshed, Wisconsin, to this phenomena. Hodge et al. (1978) suggested that a decrease in mixing height increased concentrations of Pb and Pb-210--as well as other trace metals--in air during the winter at La Jolla, California. If mixing heights were known and Pb concentrations normalized to them, it would probably produce a smoother time-concentration plot.

Atmospheric concentrations of Po-210 were highly variable, ranging between 3 and 28 dpm/10^{3}m^3. A few times during the year Po-210 was not detected in the air. This was expected since the source of Po-210 from the earth's surface to the atmosphere is not constant. Moore et al. (1976) estimated that at least 60% of Po-210 in air over the continental United States is associated with resuspended soil dust particles. If this is the case, sporadic variations in levels of unsupported Po-210 would likely be observed in the atmosphere. The concentration of supported Po-210 in the atmosphere also is variable and depends on the removal rate of aerosol Pb-210 to the earth's surface (Moore et al. 1976). Since aerosol residence times in the troposphere vary from a few days to several weeks (Poet et al.

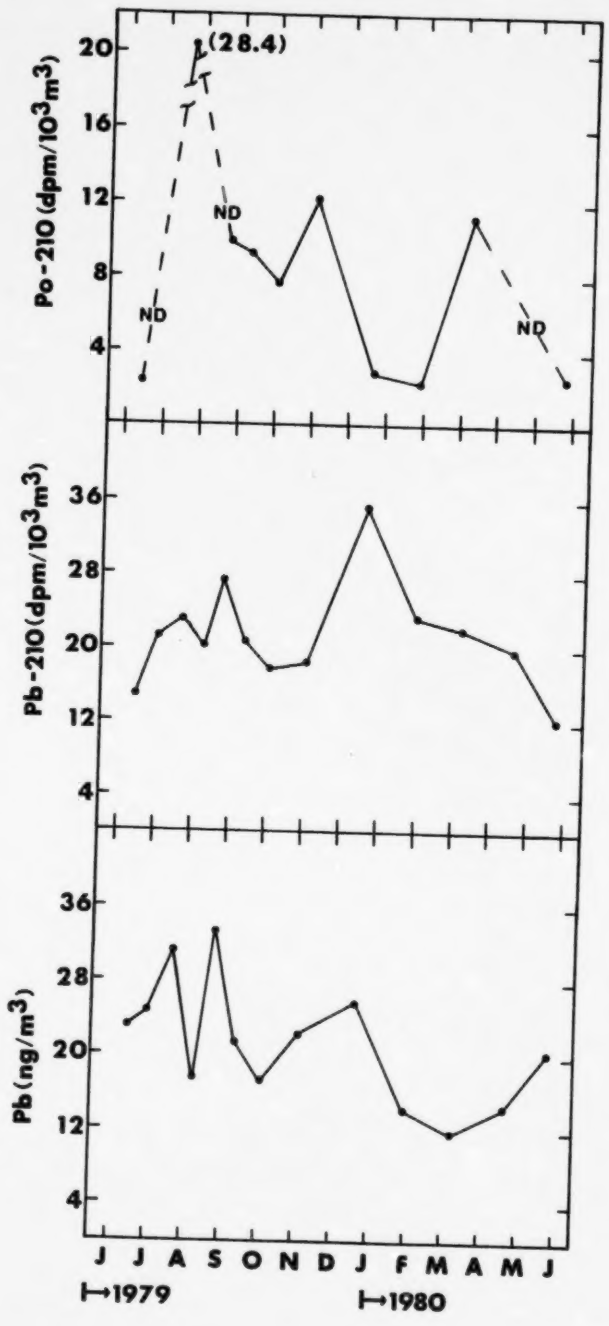


Figure 4. Atmospheric concentrations near ground level as a function of time at Vilas County, Wisconsin.

1972), supported Po-210 levels vary as well. These combined effects are the most probably cause for fluctuations in aerosol Po-210 concentrations.

The average metal concentrations for eight sampling intervals during 1979 to 1980 are shown as a function of particle size (stage number) in Table 1. These mean concentrations also are depicted in Figure 5. It is evident that the later stages of the impactor collected the largest amounts of Pb, Pb-210, and Po-210. This suggests that these metals are associated with aerosol particles of < 1 µm in diameter. The aerodynamic cutoff diameters corresponding to 50% collection efficiency with the Sierra impactor: stage 1 (8.4 µm), stage 2 (3.6 µm), stage 3 (2.0 µm), stage 4 (0.97 µm), stage 5 (0.52 µm), and the backup (0.49 µm). These theoretical cutoff diameters are quoted by the manufacturer for a glass fiber filter collection substrate and a mass flow of air of 1.1 m^3/min. Sievering et al. (1978) found that cellulose collection substrates--such as those used in this study--may have different cutoff diameters than those cited previously. Particle bounceoff and re-entrainment under conditions of low relative humidity are thought to cause an unknown amount of overlap in particle collection efficiency between successive stages of the impactor (Willeke 1975, Sievering et al. 1978). It was beyond the scope of this study to investigate this phenomena and assess its potential influence on measured concentrations and estimates of mass median equivalent diameters (MMD).

TABLE 1. AVERAGE METAL CONCENTRATIONS (MEAN ± S.D.) AS A FUNCTION OF PARTICLE SIZE (N = 8)

Stage	AL (ng/m^3)	Pb (ng/m^3)	PB-210 ($dpm/10^6m^3$)	PO-210 ($dpm/10^6m^3$)
1	32 ± 24	0.5 ± 0.2	134 ± 46	127 ± 91
2	25 ± 13	0.9 ± 0.4	215 ± 130	256 ± 283
3	14 ± 16	1.2 ± 0.5	379 ± 124	315 ± 137
4	16 ± 14	1.9 ± 0.8	1,360 ± 1,313	1,372 ± 1,046
5	13 ± 12	3.6 ± 1.3	2,562 ± 1,671	2,247 ± 1,990
Backup	35 ± 18	10.3 ± 4.2	11,499 ± 4,637	3,423 ± 1,387
∑	135	18.4	16,149	7,767
MMD[a]	1.7	0.55	0.40	0.65

[a] Mass median equivalent diameter (µm).

The representative size distribution of Pb shown in Figure 5 is similar to size distributions reported for Pb in urban areas of the United States (Lee et al. 1972, Gladney et al. 1974, Paciga et al. 1975, Davidson 1977) and over the Atlantic Ocean by Duce et al. (1976). In contrast to Pb, Al

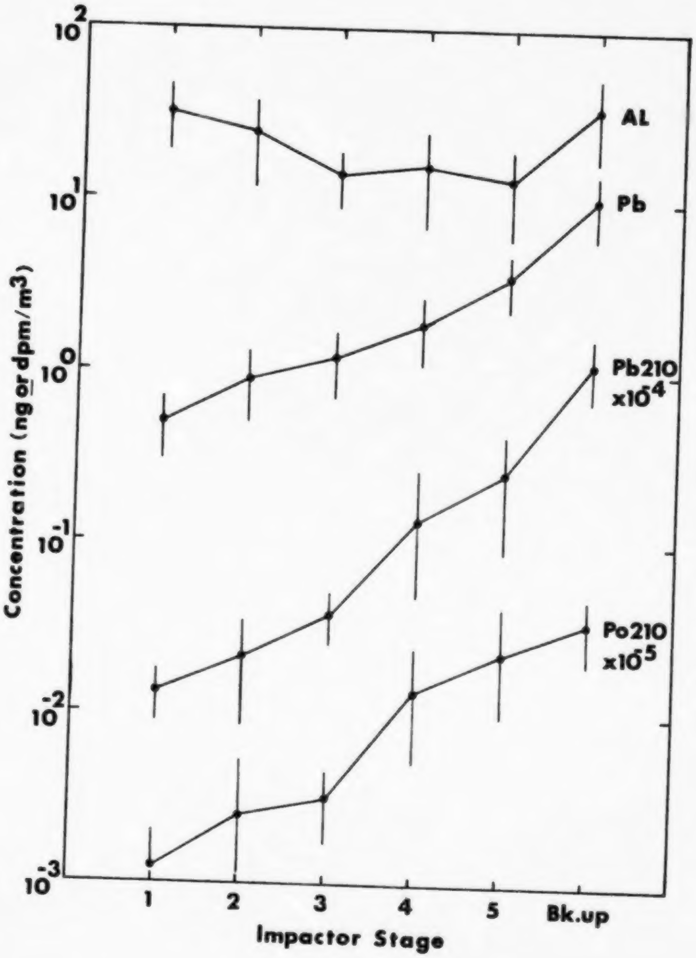


Figure 5. Average atmospheric concentrations (n=8) for 1979 to 80 as a function of impactor stage. (See Table 1).

concentrations did not appear to vary significantly with particle size. Such a monotonous size distribution is commonly observed for Al (Paciga et al. 1975, Duce et al. 1976). The mass median equivalent diameter (MMD) was 1.7 μm for Al and 0.55 μm for Pb, consistent with the general concensus that the MMD for Al is about 1 to 4 μm and is $\leq$0.5 μm for Pb (Lee et al. 1972, Colovos et al. 1974, Rahn 1976, Davidson 1977, Nraigu 1978).

The representative size distributions of Pb-210 and Po-210 are depicted in Figure 5. Results from this study indicate that the MD for Pb-210 is near 0.40 μm and 0.65 μm for Po-210. There appear to be no other estimates of MMDs reported for Pb-210 or Po-210.

Average elemental mass concentrations are presented as a function of particle size in Table 2. The mean concentrations for aerosol which has not been size differentiated are shown for comparison. Mass concentrations (i.e., mg/g or dpm/g) of Pb, Pb-210, and Po-210 increase as the smaller particle sizes are approached on the later stages of the impactor. The effect seems to be most pronounced for Pb-210 where the dpm/g value on the backup filter is more than twice the dpm/g value of stage 5. Aluminum mass concentrations (μg/g) are highest on stages 1 and 2 which suggests that this Al is associated with larger (>5 μm) crystal type material (Rahn 1976). Mass concentrations of Al on the other stages do not vary significantly and average 30% lower than stages 1 and 2.

TABLE 2. AVERAGE ELEMENTAL CONCENTRATIONS AS A FUNCTION OF PARTICLE SIZE (N = 8)

STAGE	Al (mg/g)	Pb (mg/g)	Pb-210 (dpm/g)	Po-210 (dpm/g)
1	9.6	0.33	72	74
2	9.4	0.69	123	134
3	7.0	0.89	273	391
4	5.3	1.3	436	627
5	4.5	2.5	1,210	1,100
Backup	5.3	3.9	2,750	1,210
Hi-Vol[a]	10.8	1.9	1,800	782

[a] Average elemental concentrations for hi-volume aerosol which was not size differentiated (See Appendix B).

Additional information on particle size relationships is contained in Table 3 where average elemental and isotopic ratios are given as a function of particle size. The highest Pb-210:Pb ratio was found on the backup filter. This indicates, in addition to the other particle size relationships, that Pb-210 is associated with very small aerosol, probably

<0.5 μm. The low ratio Po-210: Pb-210 on the backup filter compared to the ratio of about 1.0 on stages 1 to 5 suggests the same thing.

Lead also appears to be associated with submicron aerosol. The MMD of Pb (0.55 μm) suggests that it should be associated with aerosol collected primarily by stage 5 and the backup filter. The Pb:Al ratios of these fractions are the same (Table 3). An average enrichment factor of about 1800 on these stages indicates that the particles are greatly enriched with Pb probably of anthropogenic origin (Colovos et al. 1974, Rahn 1976, Duce et al. 1976).

TABLE 3. AVERAGE ELEMENTAL AND ISOTOPIC RATIOS AS A FUNCTION OF PARTICLE SIZE

Stage	Pb-210:Pb (dpm/mg)	Po-210:Pb-210	Pb:Al	Pb-210:Al (dpm/mg)	Po-210:Al (dpm/mg)	EF[a] (Pb)
1	268	0.95	0.02	4	4	98
2	239	1.2	0.04	9	10	225
3	316	0.83	0.09	27	23	536
4	716	1.0	0.12	85	86	743
5	712	0.88	0.28	197	173	1,732
Backup	1,116	0.30	0.29	329	98	1,840
Total	878	0.48	0.14	120	58	888

[a] Enrichment factor.

RAINFALL MEASUREMENTS

The concentrations of Pb and Pb-210 in rainfall are illustrated in Figure 6. The activity of Pb-210 in rain is corrected for decay to the midpoint of the sampling interval. The weighted mean concentration of Pb was 7.9 μg/kg and 17.4 dpm/kg for Pb-210. Lead concentrations in rain were <10 μg/kg, except for a brief period in early August when the concentration was ~ 20 μg/kg. Mid-summer concentrations of Pb-210 were higher than those in spring or early fall. A steady increase in Pb-210 concentration was observed between June and August. Thereafter, the concentration decreased rapidly to around 13 dpm/liter, which is the same concentration observed during early June.

There is no apparent statistical relationship ($|r|<0.5$) in these data between Pb or Pb-210 concentration and the amount of rainfall. Several authors have observed a statistical relationship between precipitation volumes and Pb concentrations (Chow and Earl 1970, Parungo and Rhea 1970, Ter Haar et al. 1967). Stolzenburg (1979) observed an inverse relationship

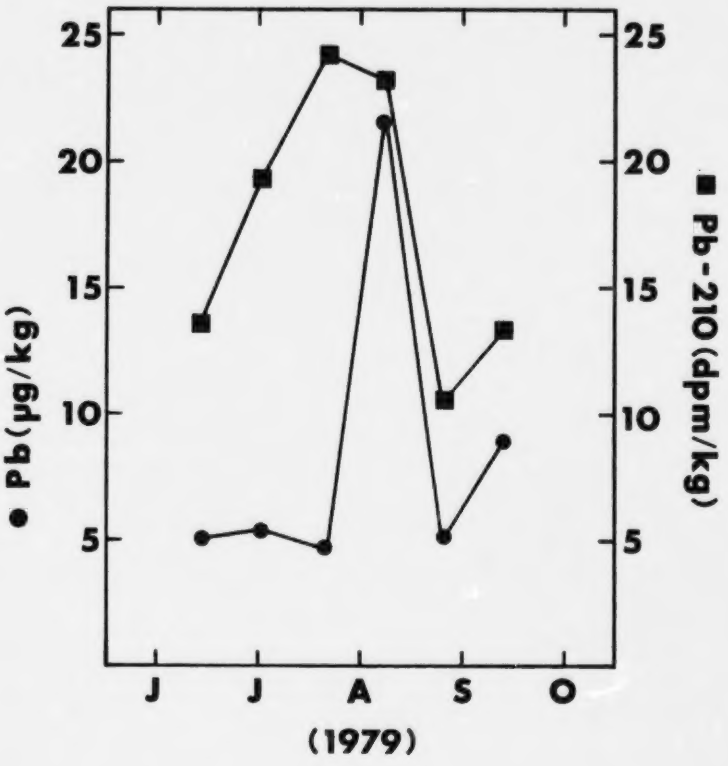


Figure 6. Concentrations of Pb and Pb-210 in rainfall as a function of time at Vilas County, Wisconsin.

on one occasion between Pb concentration and the amount of rain falling on the Menomonee River Watershed Wisconsin. Turekian et al. (1977) suggested that at some locations Pb-210 concentration is correlated positively with amount of rainfall. It is not appropriate to examine such a relationship in the samples collected for this study since individual events were not sampled. Instead, the data represent integrated rainfall events over a 2-week time interval. The data were collected in this manner since integrated samples over short time intervals are best for estimating wet deposition (Turekian et al. 1974).

In a study similar to the present one, Elias et al. (1975) measured Pb concentrations in air and rainfall at the Yosemite subalpine study area. They found Pb concentrations in rain of about 10 μg/kg where atmospheric Pb concentrations averaged 25 ng/m^3. This is essentially the same relationship between average Pb concentrations in air (21 ng/m^3) and rain (8 μg/kg) observed in this research.

Polonium-210 was detected in rain only during late spring and early fall (see Appendix B). Concentrations of Po-210 were between 0.2 and 2 dpm/liter during these periods. Poet et al. (1972) observed 0.3 to 1 dpm/liter of Po-210 in rain at Boulder, Colorado. Francis et al. (1970) found Po-210 concentrations of 0.4 to 7 dpm/liter in rain at Madison, Wisconsin. This limited set of data suggests that the average concentration of Po-210 in rain over the midwestern states may be in the range of a few tenths to several dpm/liter. High concentrations (>1 dpm/liter) may be related to periods of high dust resuspension in the atmosphere. The 1.8 dpm/liter concentration of Po-210 observed in early June at Vilas County, Wisconsin may reflect this phenomena.

CRYSTAL LAKE TEMPERATURE PROFILES

The temperature profiles observed during 1979 to 1980 for Crystal Lake are depicted in Figure 7. The profiles indicate that Crystal Lake developed a stable stratificiation. Metalimnetic temperature gradients were strong (~ 3°C/m at 6 to 8 m) and metalimnetic temperatures varied little from July to early September. Erosion of the thermocline was primarily by downward turbulent mixing of heat.

Sampling of the water column began on 5 June 1979 when the water column was essentially isothermal. A little more than 2 weeks later the lake was thermally stratified. The epilimnion continued to increase in temperature and evidence exists for the formation of a double thermocline by 11 July 1979. The epilimnion reached its maximum temperature about mid-July.

By August 1979 the thermocline had deepened and the metalimnion was subject to some heating. The epilimnion had begun to cool as early as mid-August, but there was little metalimnetic heating at this time. Finally, by mid-September the thermocline was rapidly deteriorating with intense heating occurring downward into the hypolimnion. A few weeks later the lake was essentially isothermal with a slight temperature gradient existing near the

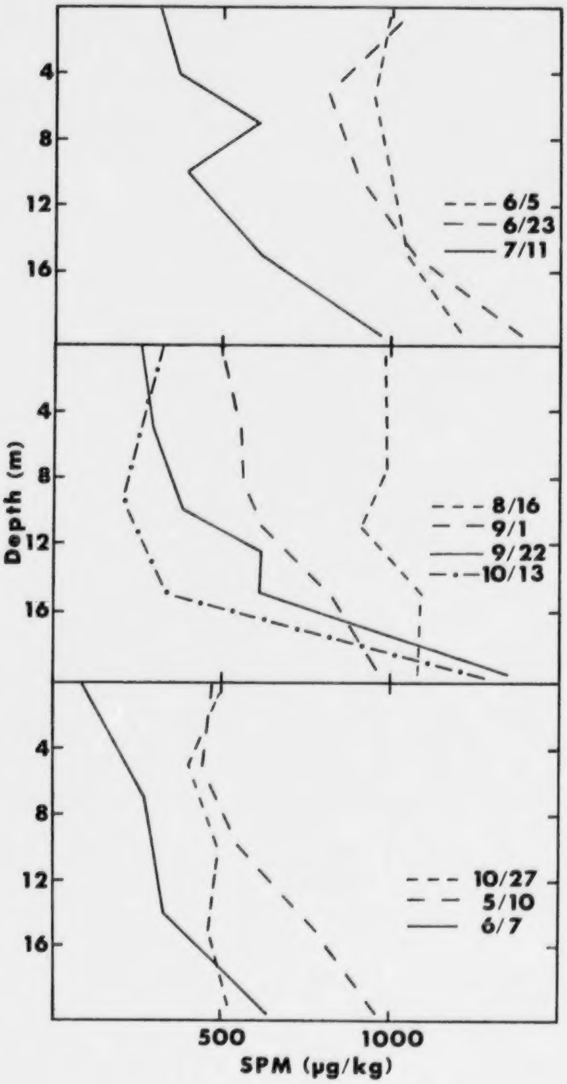


Figure 7. Temperature profiles for Crystal Lake (1979 to 80).

bottom. Complete isothermal conditions were prevalent by 27 October 1979. The lake was ice covered about 3 weeks later.

Water sampling continued after ice-out in 1980. The temperature profile observed on 10 May 1980 was obtained about 2 weeks after ice-out. The upper surface water showed vague signs of heating; but below 10 m the temperature was isothermal, around 2°C. By early June the temperature of the water column had risen significantly and thermal stratification probably occurred shortly thereafter. Due to the unusually warm spring (1980) the surface water was much warmer in June 1980 than in June 1979.

CRYSTAL LAKE SUSPENDED PARTICULATE MATTER PROFILES

The suspended particulate matter (SPM) profiles observed during 1979 to 1980 for Crystal Lake are depicted in Figure 8. Suspended particulate matter is defined as that material retained by a 0.4 μm filter (Nuclepore). Virtually all profiles show a trend of increasing concentration with depth. Surface water SPM concentrations were generally in the range 250 to 500 μg/kg. The higher concentrations near the bottom of about 1000 μg/kg are probably the result of zooplankton migrating downward during daylight hours.

Suspended particulate matter concentrations were highly variable over the year, being as low as 100 μg/kg and approaching 1400 μg/kg at other times. The lowest concentrations always occurred in surface water, usually in the upper 1 to 2 m. Most of the spatial and temporal variation of SPM is believed to be related directly to biological activity in the water column. During unproductive periods the SPM concentration appears to vary little with depth and is only several hundred μg/kg.

On three occasions (i.e., twice in June and once in August), SPM concentrations were dramatically higher than at other times, averaging >1000 μg/kg in the entire water column. The SPM concentration during all other periods averaged about 500 μg/kg. This suggests that the higher SPM concentrations represent plankton blooms. Microscopic examination of the SPM filters confirmed that an abundance of plankton existed at these times compared to the other sampling periods.

Birge and Juday (1929) estimated that during a mid-August (20 August 1929) plankton bloom in Crystal Lake, the plankton exhibited an invariant concentration with depth of 576 ± 83 μg/liter. This is essentially the same plankton biomass estimated in the present study for 16 August 1979: mean (± S.D.) SPM on 16 August 1979 was 1008 ± 66 and non-bloom mean 474 ± 42 μg/kg; plankton biomass therefore, roughly equals 1008 - 474 = 534 ± 55 μg/kg. The good agreement between this estimate and that of Birge and Juday (1929) indicates the lake's biomass may not have changed significantly in the past 50 yr.

The SPM profiles observed during June may reflect the effect of a diatom bloom. Crystal Lake has a diverse and healthy diatom population

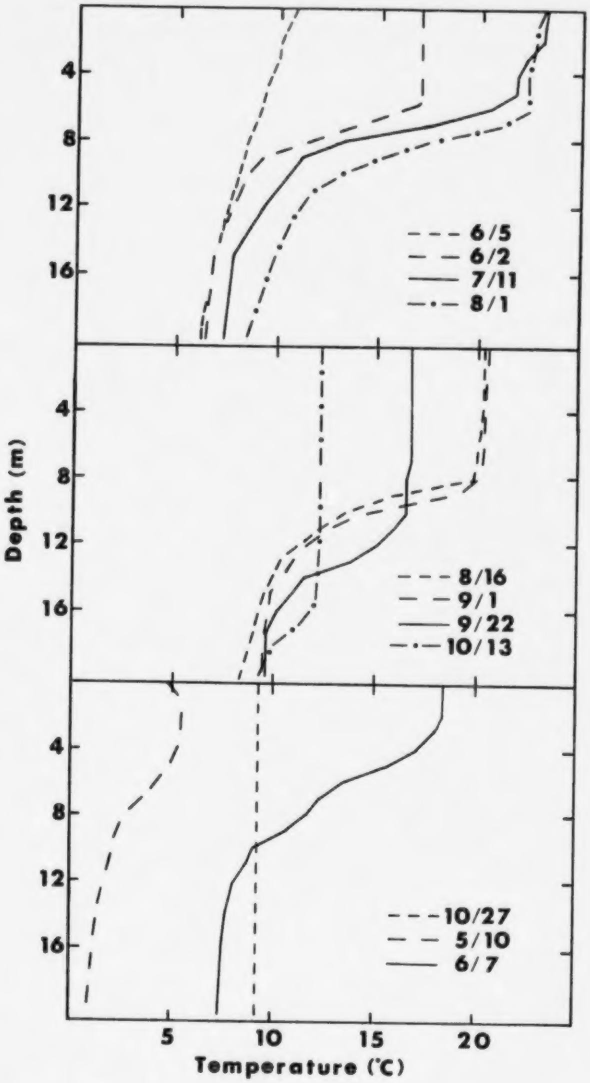


Figure 8. Suspended particulate matter profiles for Crystal Lake (1979 to 80).

(Conger 1939). However, Conger (1939) concluded that the dominant diatoms--i.e. miscellaneous genera of *Eunotia*, *Navicula*, and *Stauroneis*) are primarily epiphytic on various benthic fauna--e.g., mosses.

Microscopic examination of the 5 and 23 June 1979 filters used for determining SPM concentrations revealed that pine pollen constituted around 20% of all identifiable particles on filters spanning the entire water column. The widespread distribution in the lake and the high density of pollen on the filters suggest that pine pollen contributed to the SPM in Crystal Lake.

High-volume air samples collected during June also were examined microscopically to check for pine pollen. It was determined that pine pollen comprised the majority of the aerosol collected on the filters. Furthermore, the pine pollen identified on the air filters was identical to the pine pollen observed in the water column of Crystal Lake. These findings strongly suggest that pollen may be a significant atmospheric "episodic event-type" input to some lakes, particularly lakes situated in or near heavily forested areas.

Diatoms were not found on any of the 5 or 23 June 1979 SPM filters; but since only 1 or 2 liters of water were filtered, the lack of diatoms may be a sampling artifact. The dominant phytoplankters during June were *Staurastrum* sp. *paradoxum* (~ 80%) and *Dinobryon*. The principal zooplankters were of the genus *Rotatoria* (80%) and order Cladocera.

From this study it is difficult to accurately determine what portion of the high SPM concentration observed during June to attribute to pine pollen and to *in situ* biological production. Based on absolute numbers, plankton comprised the majority of the material in the lake during June.

During the rest of the year--termed non-bloom periods--the SPM was composed of various phytoplankters (particularly *Dinobryon* and green algae) and mixed zooplankters. Occasionally *Navicula* diatoms were observed on the filters, but they always appeared to comprise <1% of the phytoplankton. Detritus, however, constituted a significant fraction of the SPM, especially in surface waters.

PRESENTATION OF WATER COLUMN DATA

The vertical distribution of dissolved and particulate phase Pb-210 is shown as a function of depth in Figures 9 to 18. Polonium-210 concentrations are plotted as activity differences relative to parent Pb-210 activities. Positive values indicate the presence of excess Po-210 not supported by *in situ* decay of Pb-210.

Analyses have been corrected for growth or decay to the time of collection and are expressed as dpm/100 kg/min/lake water. To portray the depth distributions without the boundary effects (i.e., a 1-m thick slice of water at the surface contains more water than a 1-m slice near the bottom),

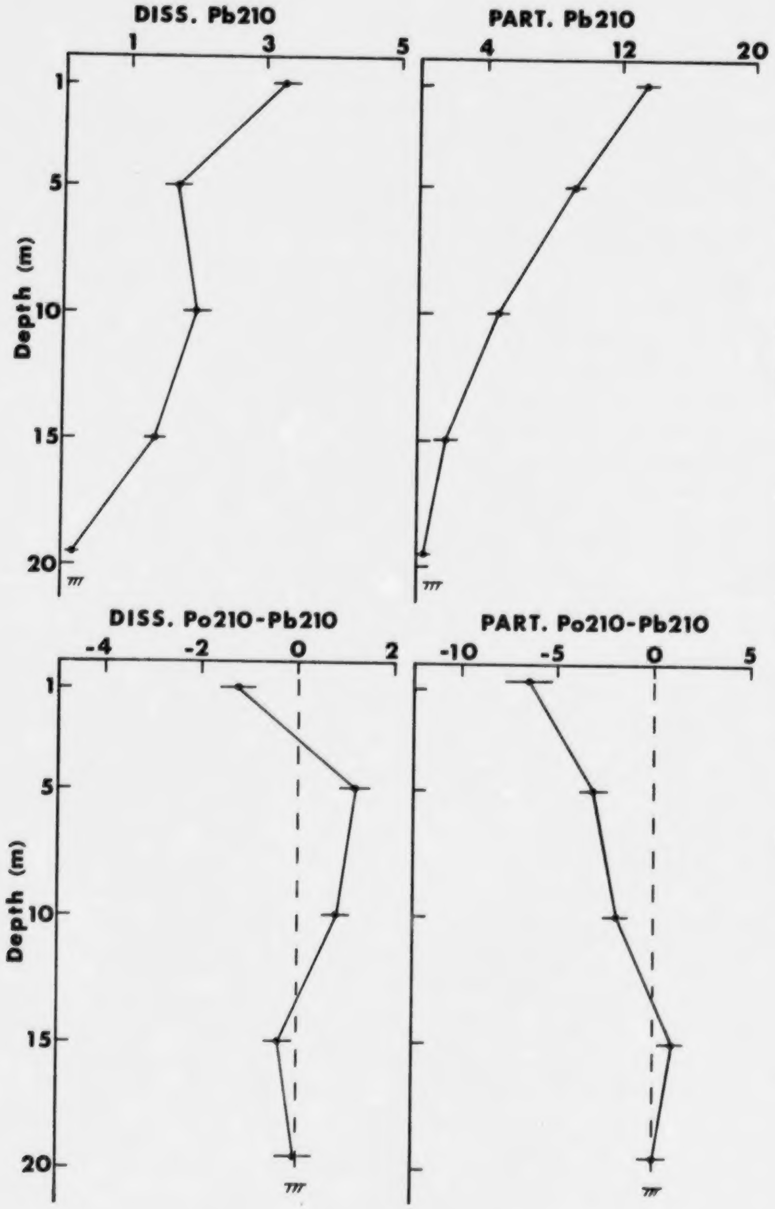


Figure 9. Vertical profiles of Pb-210 and Po-210 in Crystal Lake on 5 June 1979. Data are plotted as normalized concentrations (dpm/100 kg).

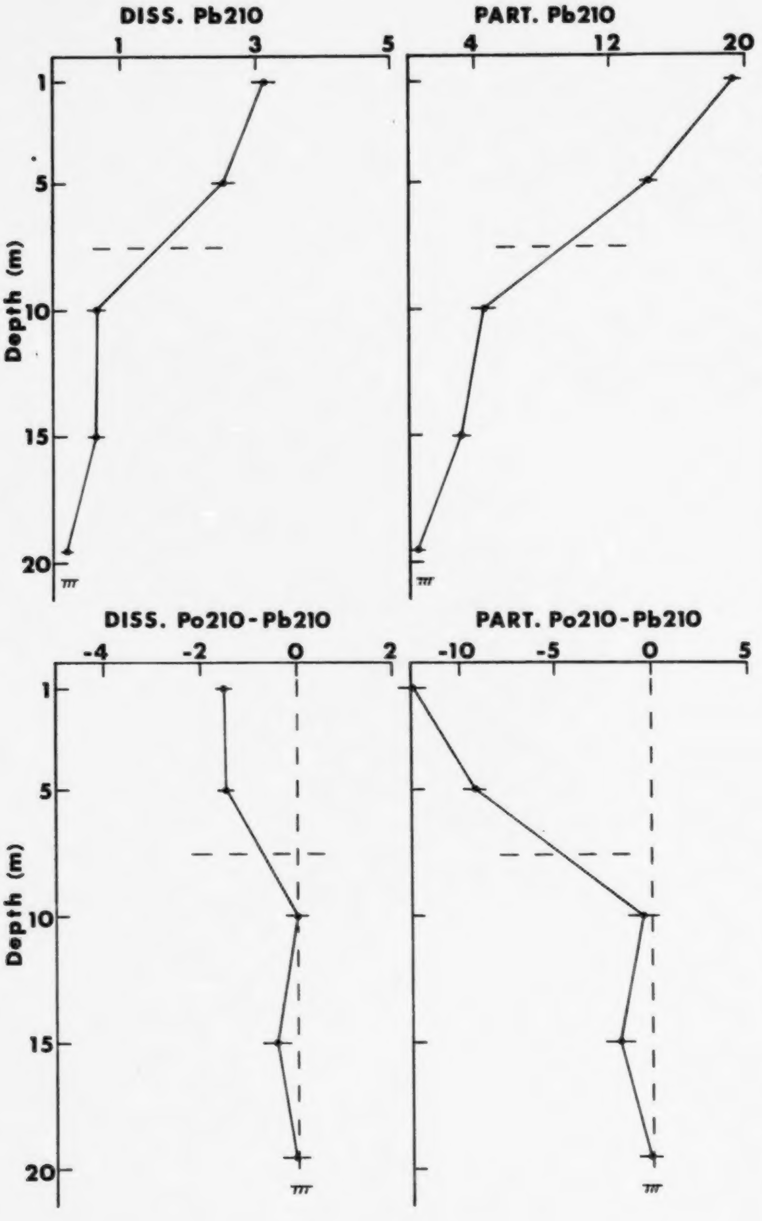


Figure 10. Vertical profiles of Pb-210 and Po-210 in Crystal Lake on 23 June 1979. Data are plotted as normalized concentrations (dpm/100 kg). Horizontal dashed line indicates approximate depth of the thermocline.

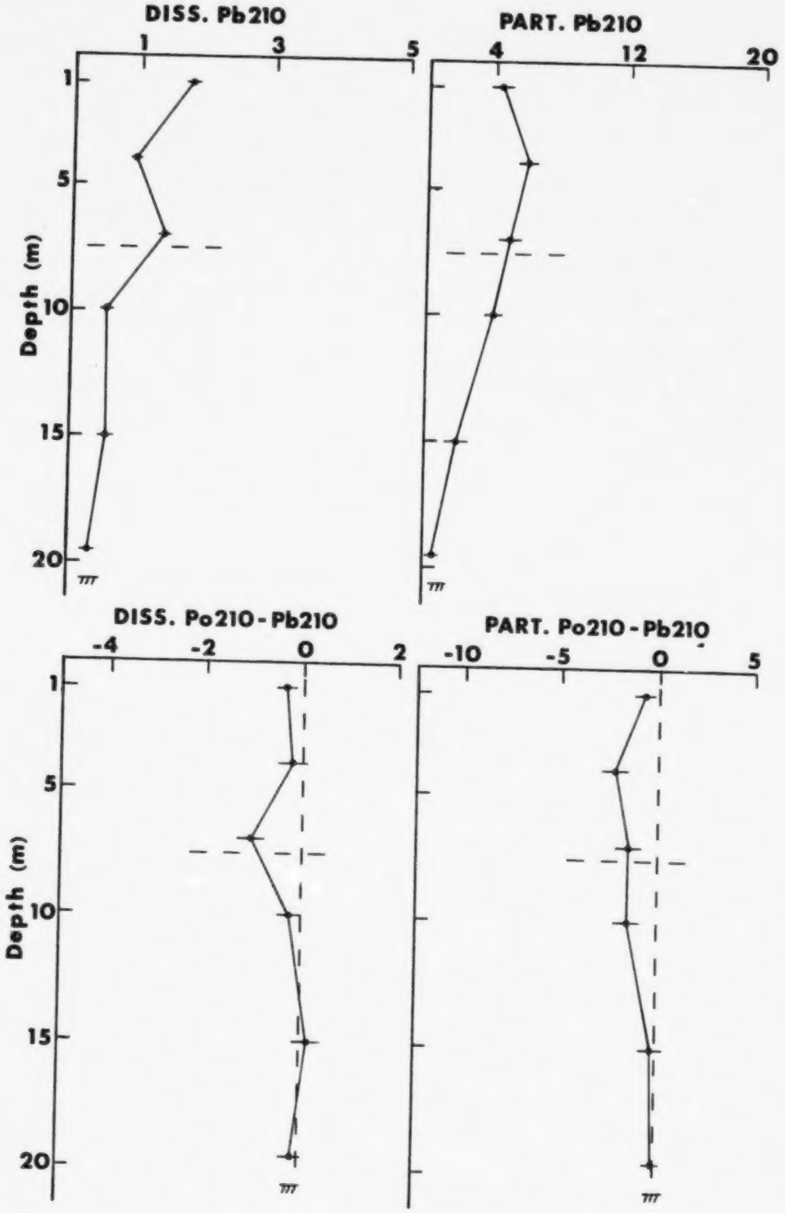


Figure 11. Vertical profiles of Pb-210 and Po-210 in Crystal Lake on 11 July 1979. Data are plotted as normalized concentrations (dpm/100 kg). Horizontal dashed line indicates approximate depth of the thermocline.

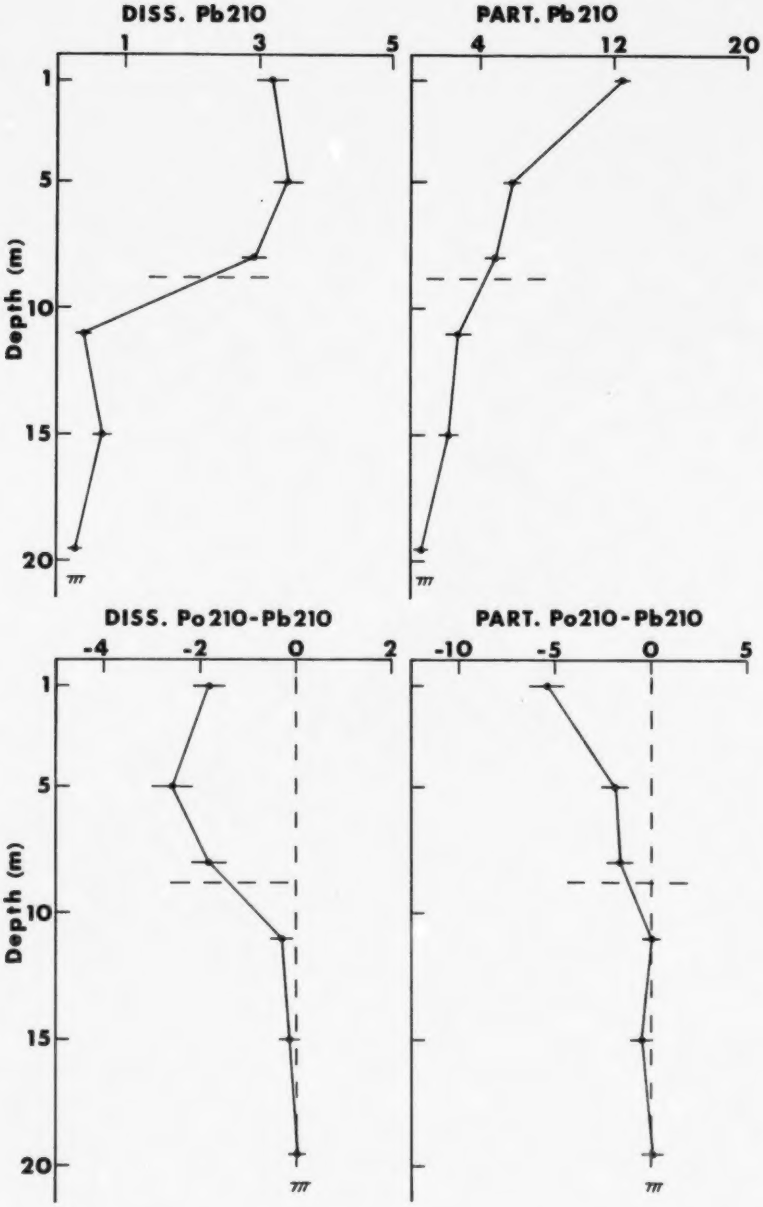


Figure 12. Vertical profiles of Pb-210 and Po-210 in Crystal Lake on 16 Aug. 1979. Data are plotted as normalized concentrations (dpm/100 kg). Horizontal dashed line indicates approximate depth of the thermocline.

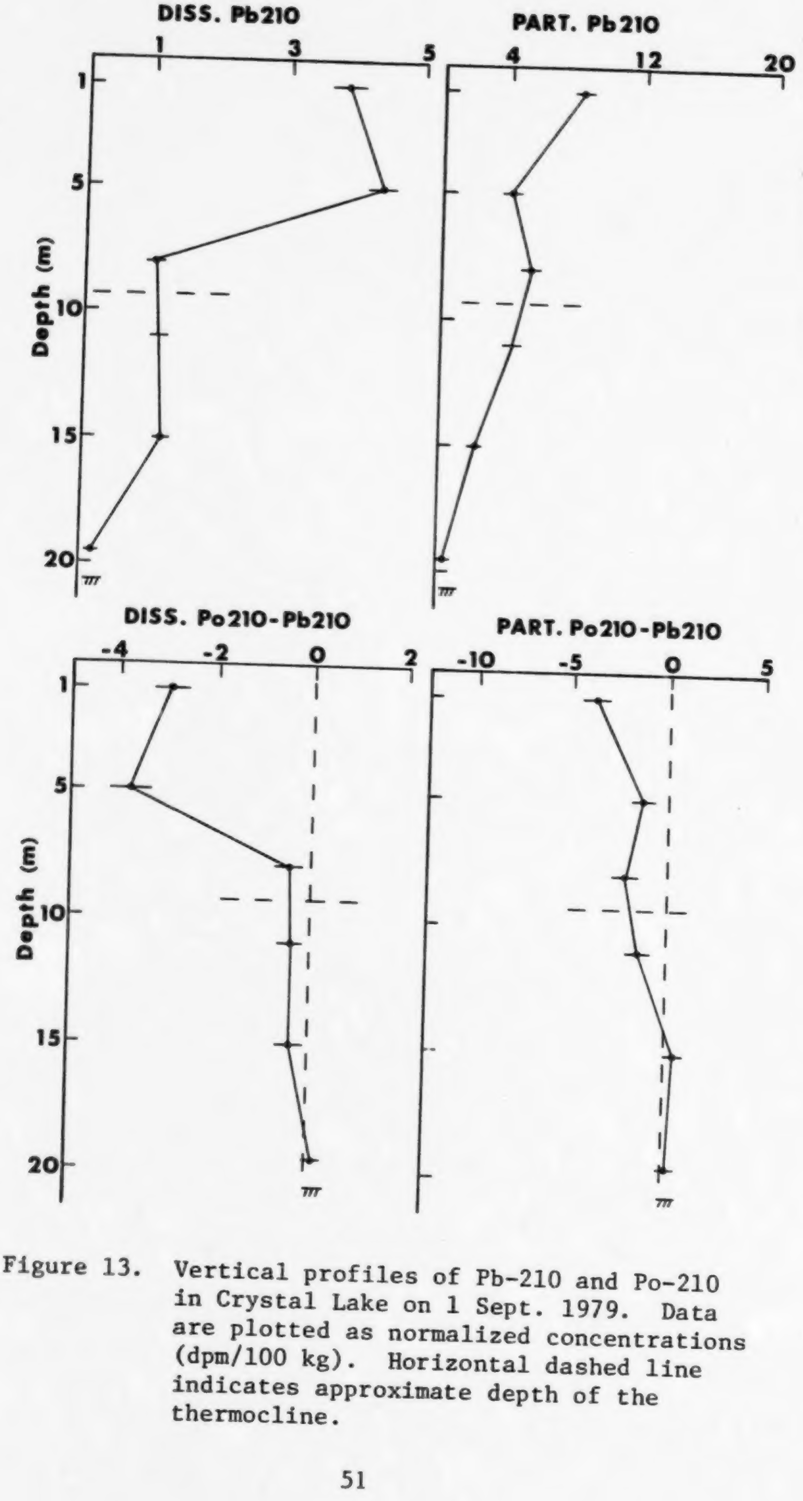


Figure 13. Vertical profiles of Pb-210 and Po-210 in Crystal Lake on 1 Sept. 1979. Data are plotted as normalized concentrations (dpm/100 kg). Horizontal dashed line indicates approximate depth of the thermocline.

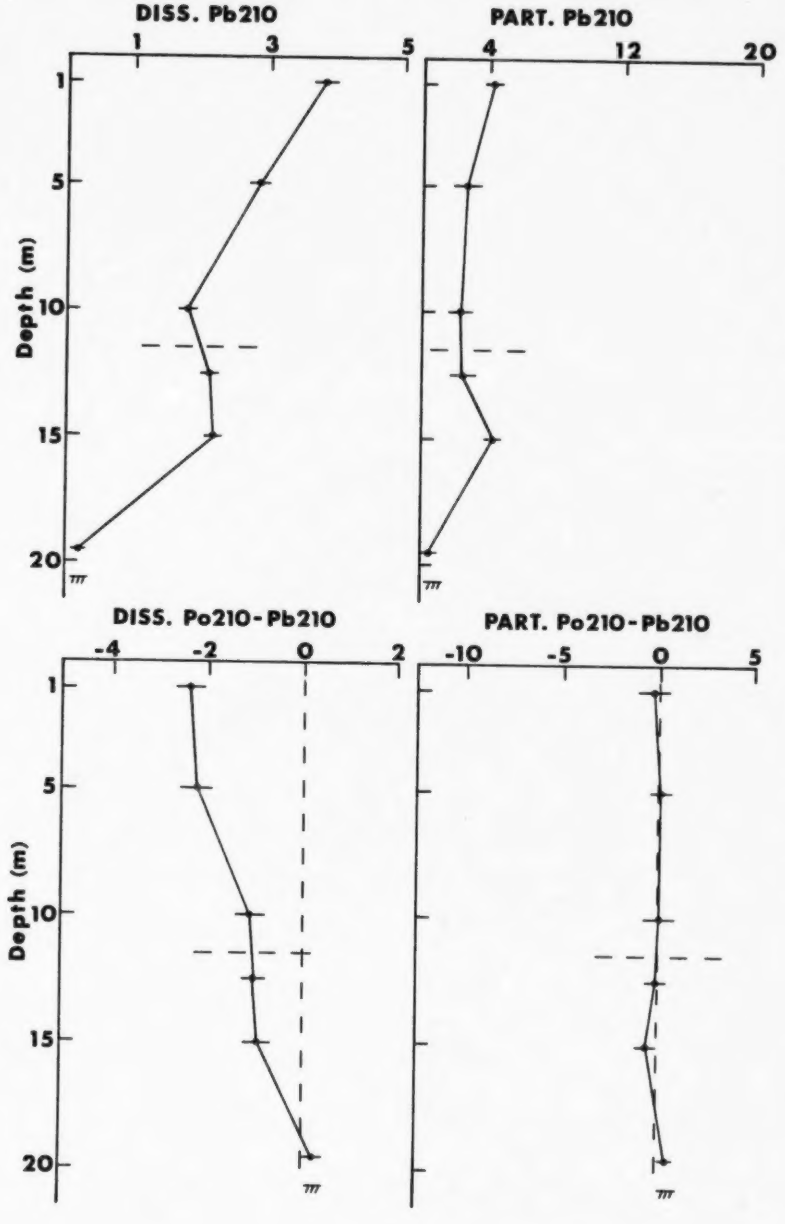


Figure 14. Vertical profiles of Pb-210 and Po-210 in Crystal Lake on 22 Sept. 1979. Data are plotted as normalized concentrations (dpm/100 kg). Horizontal dashed line indicates approximate depth of the thermocline.

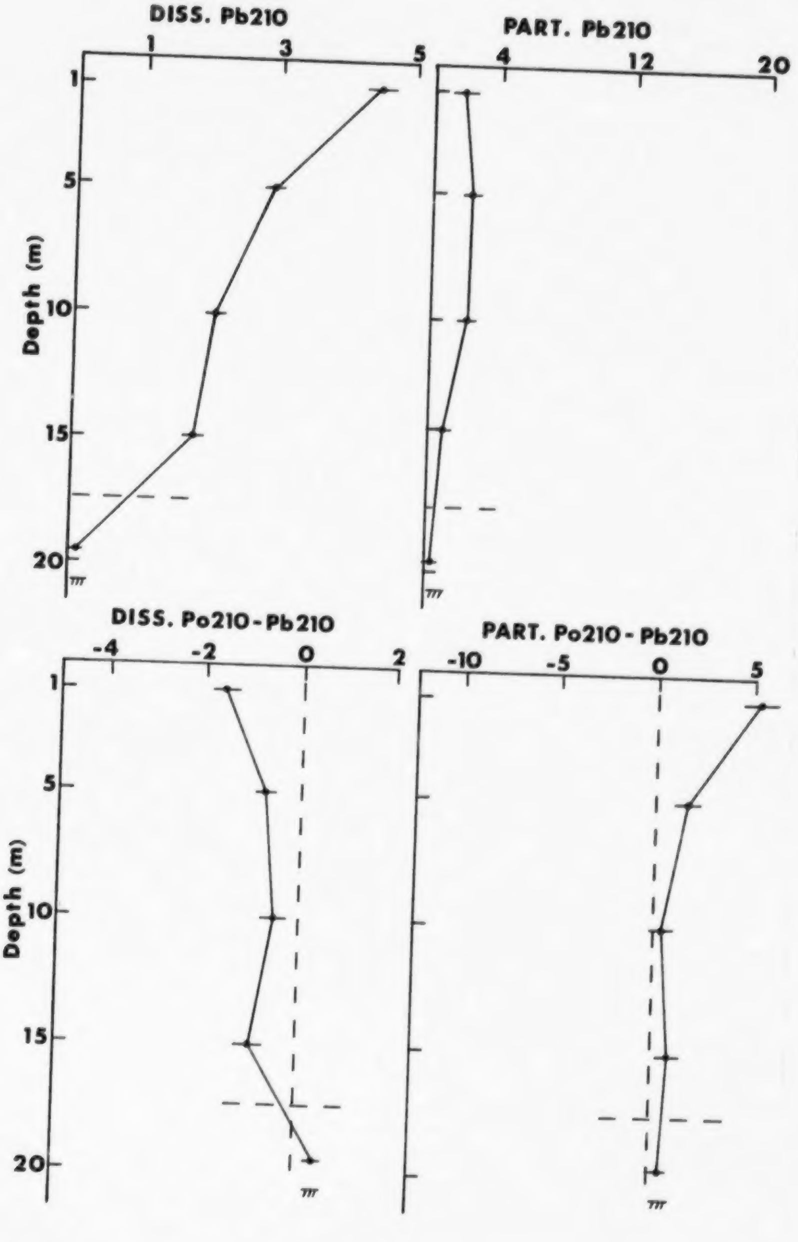


Figure 15. Vertical profiles of Pb-210 and Po-210 in Crystal Lake on 13 Oct. 1979. Data are plotted as normalized concentrations (dpm/100 kg). Horizontal dashed line indicates approximate depth of the thermocline.

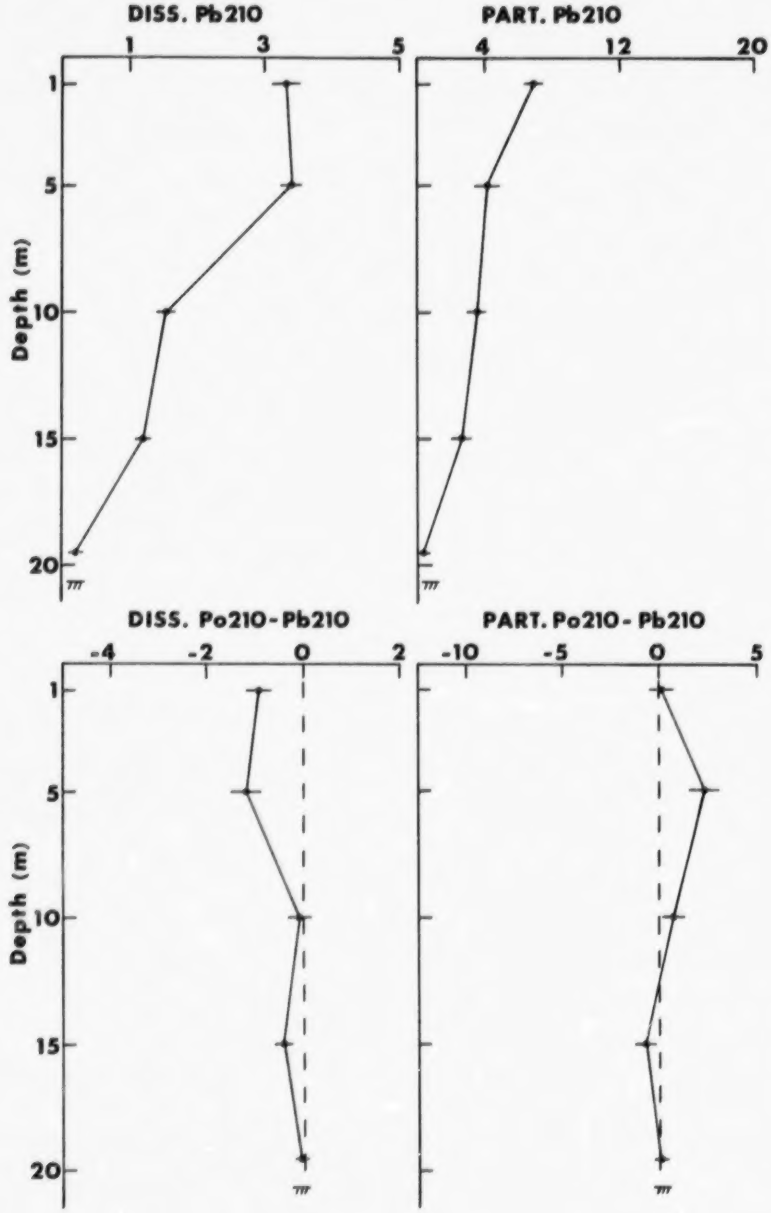


Figure 16. Vertical profiles of Pb-210 and Po-210 in Crystal Lake on 27 Oct. 1979. Data are plotted as normalized concentrations (dpm/100 kg).

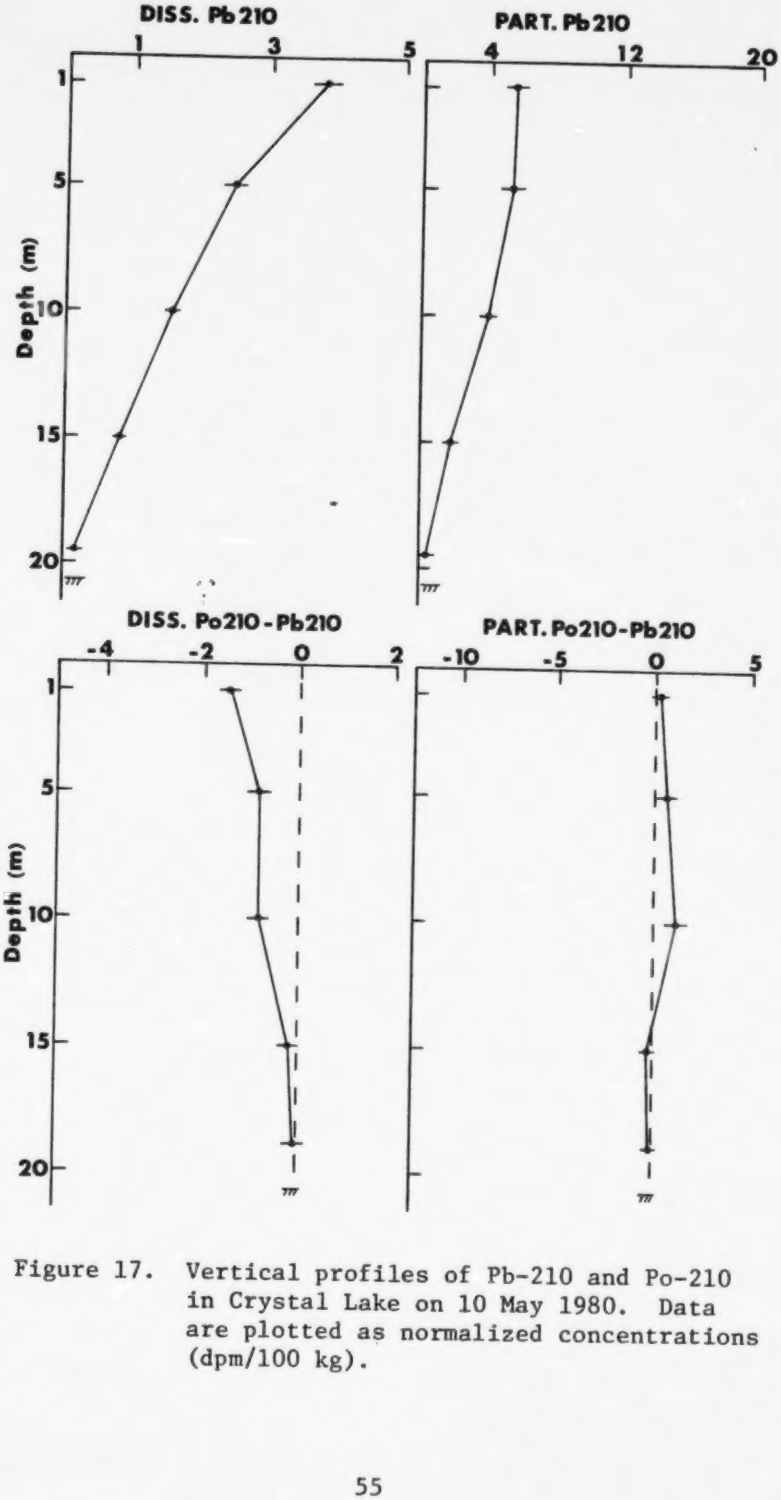


Figure 17. Vertical profiles of Pb-210 and Po-210 in Crystal Lake on 10 May 1980. Data are plotted as normalized concentrations (dpm/100 kg).

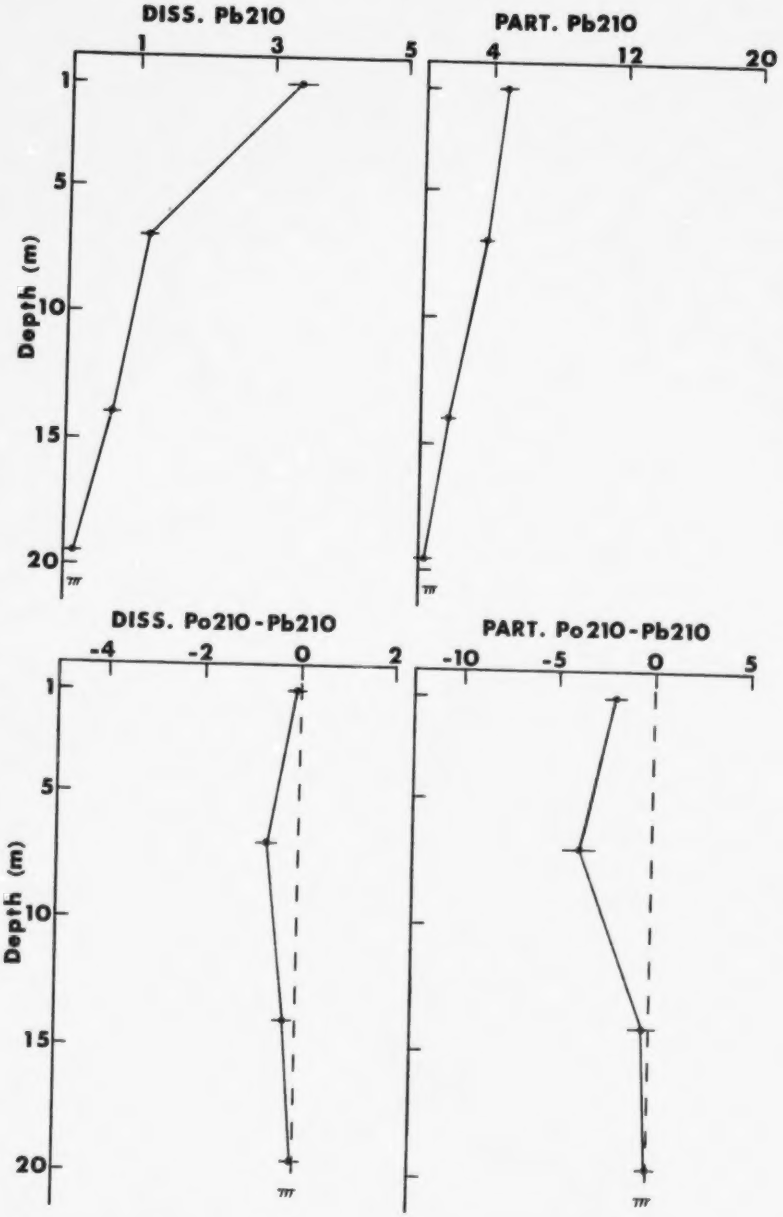


Figure 18. Vertical profiles of Pb-210 and Po-210 in Crystal Lake on 7 June 1980. Data are plotted as normalized concentrations (dpm/100 kg).

measured concentrations were normalized by multiplying them by the ratio of lake area at sampling depth to lake surface area. Concentrations plotted in Figures 9 to 18 are expressed in this manner. Analytical results for Pb-210 and Po-210 are given in Appendix B.

The distinction between "dissolved" and "particulate" activity is based on retention or non-retention by the filters. Duplicate water samples were collected on several occasions and analyzed for Pb-210 and Po-210. Total activities for unfiltered and filtered (sum of dissolved and particulate activities) samples always agreed within the bounds of 1σ counting statistics. Consequently the sum of dissolved and particulate activities was a good indication of total Pb-210 or Po-210 activities (see Section 9).

Error bars indicated on the analytical results plotted in Figures 9 to 18 reflect uncertainty due to counting and analytical precision. An idea of the uncertainty attributed to analytical precision was obtained from the standard deviation of recoveries of Po-208 spikes at "high" and "low" activity levels. Dissolved and particulate samples were divided into two groups based on their total activity. These groups were: Dissolved, <0.3 dpm or >0.3 dpm; and particulate, <0.7 dpm or >0.7 dpm. The overall analytical precision was estimated based on the average precision of Po-208 spike recoveries in each of the four groups. Counting statistics for individual samples were based on random counting error as described previously.

DISTRIBUTION OF Pb-210

Ordinarily more than 60% of the Pb-210 in Crystal Lake is in the particulate phase. Surface water (0 to 10 m) concentrations of Pb-210 in dissolved and the particulate phase were always higher than those in deep water (10 to 21 m). The higher surface concentrations are probably maintained by delivery of unsupported Pb-210 produced in the atmosphere by Rn-222 decay. The atmosphere appears to be the principal source of Pb-210 to Crystal Lake. This means the majority of Pb-210 in the lake is unsupported.

In general, particulate phase Pb-210 varied more than dissolved Pb-210. Fluctuations in total Pb-210 were, therefore, usually brought about by changes in particulate Pb-210. Much of the temporal variation in particulate Pb-210 concentrations probably is associated with changes in the lake's biomass. This is especially true in surface water during the productive spring and summer stratified periods.

Particulate Pb-210 concentrations were lowest when the lake was not stratified but still showed a trend of decreasing concentration going from surface to bottom. During the unstratified period particulate phase Pb-210 decreased from an average of 4 dpm/100 kg in surface water to $\leq$0.5 dpm/100 kg near the sediment. About 65% of the Pb-210 was in the particulate phase and there was no discernible deviation from this distribution in the water column.

Particulate Pb-210 was highly variable in surface water during the stratified period. Concentrations varied from about 2 to 20 dpm/100 kg. Uncommonly high surface concentrations (20 dpm/100 kg) were observed during June and mid-August. More than 80% of the Pb-210 was in the particulate phase at these times. As discussed previously, the high suspended particulate matter concentrations strongly suggest that plankton blooms occurred during these periods. Freshwater plankton are known to concentrate trace metals to a high degree and concentration factors (i.e., concentration in plankton:concentration in water) of $> 10^3$ have been observed in this study and by Holm (1978). The high particulate Pb-210 concentrations observed in Crystal Lake may reflect plankton Pb-210 concentrations.

Deep water (10 to 21 m) particulate Pb-210 concentrations were lower and not as variable as surface water concentrations. The lowest concentrations always occurred near the bottom and usually were in the range 0.5 to 1.0 dpm/100 kg. Concentrations at depths of 10 to 15 m varied from 2.0 to 4.0 dpm/100 kg. As in surface water, deep water particulate Pb-210 concentrations were highest during suspected plankton bloom periods.

Dissolved Pb-210 concentrations in surface water varied little with time and were ordinarily around 3.0 dpm/100 kg. Deep water concentrations ranged from 0.2 to 2.0 dpm/100 kg with the lowest concentrations occurring near the bottom sediments.

Dissolved concentrations of Pb-210 increased steadily toward the end of the stratified period (i.e., after 1 September 1979). Suspended particulate matter concentrations decreased during this time and may be partially responsible for the higher dissolved concentrations. In addition, the lower suspended particulate matter concentrations indicate that biological productivity was decreasing. This might also tend to favor higher dissolved concentrations since dissolved deficiencies in productive ocean waters have been attributed to rapid removal by plankton (Shannon et al. 1970, Turekian et al. 1974).

Dissolved concentrations of Pb-210 varied more during the stratified period than during the unstratified period. This is probably due to the interaction of dissolved Pb-210 with plankton during the biologically productive summer months. During the unstratified period, dissolved phase Pb-210 averaged 35% of the total Pb-210. This suggests that a steady-state condition with respect to supply and removal of Pb-210 may be maintained during the biologically less productive months.

DISTRIBUTION of Po-210

The depth distribution of Po210-Pb210 disequilibria in Crystal Lake is illustrated in Figure 19. With the exception of a few spurious points, dissolved Po-210 activities always showed a deficiency relative to Pb-210. The surface water exhibited the greatest deficit, which is probably the result of rapid removal of Po-210 by plankton. Similar Po-210/Pb-210 disequilibria have been observed in the surface ocean and are attributed to

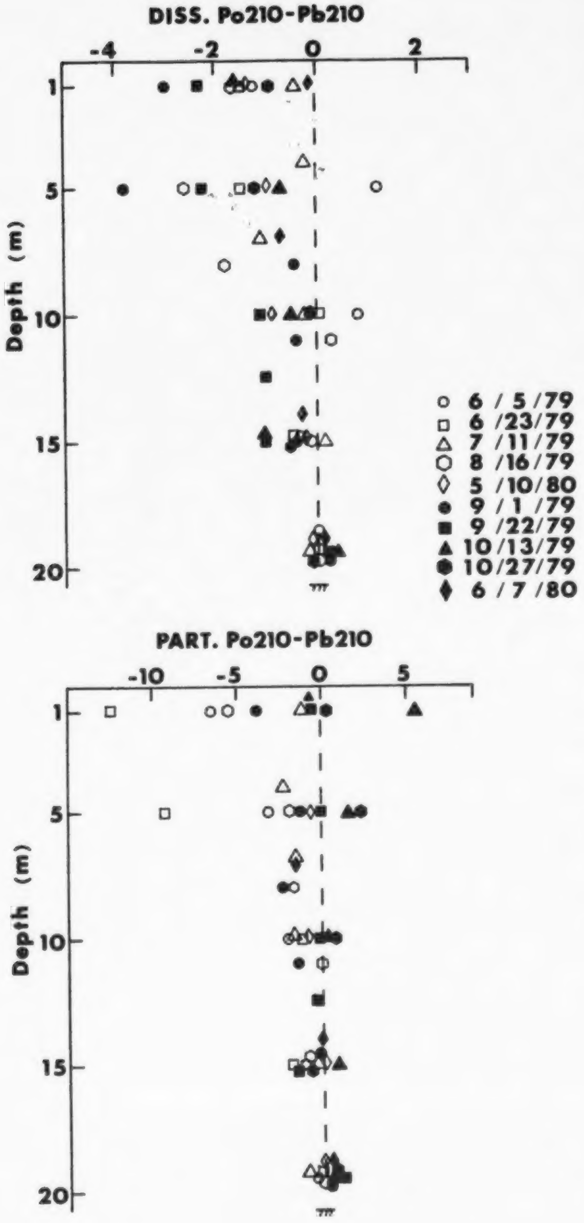


Figure 19. Summary of Po-210/Pb-210 disequilibria in Crystal Lake for all sampling dates. Data are plotted as normalized concentrations (dpm/100 kg).

rapid removal of Po-210 by biosphere activities (Shannon et al. 1970, Turekian et al. 1974, Bacon et al. 1976, Bacon 1977).

Particulate phase Po-210 activities also showed a deficit, but excess Po-210 was present on several occasions. Excess particulate Po-210 was commonly observed a few meters above the sediment. This excess Po-210 is thought to be related to activities of migrating zooplankton.

Histograms of Po-210:Pb-210 activity ratios are shown in Figure 20 and statistics are summarized in Table 4. Dissolved Po-210 activities were less than those of Pb-210 by about 21%. This difference is significant at the 95% confidence level. Particulate phase activities, however, are not significantly different at the 95% confidence level. Apparently the dissolved phase deficiency is not balanced by a particulate phase excess. Total Po-210 activities are consequently less than Pb-210 activities by about 11% (significant at the 95% confidence limit). This suggests that Po-210 is removed from the water column to maintain the dissolved deficit. Interaction witn living and dead particulate matter probably expedites removal. Thomson and Turekian (1976) observed a mean activity ratio Po-210:Pb-210 of 0.89 in an upwelling (productive) area of the eastern South Pacific. They attributed the depletion of Po-210 relative to Pb-210 to active scavenging of Po-210 from surface water by biological activity.

Table 4. SUMMARY OF Po-210:Pb-210 ACTIVITY RATIOS IN CRYSTAL LAKE. CONFIDENCE LIMITS FOR THE MEAN WERE CALCULATED AT THE 95% LEVEL

	Median	Mean
Dissolved	0.63	0.79 ± 0.18
Particulate	0.89	1.04 ± 0.18
Total	0.82	0.89 ± 0.13

DISTRIBUTION OF Rn-222 AND Ra-226

The fact that Crystal Lake is a seepage lake suggests that a source of Pb-210 to the lake may be groundwater. Groundwater contains Ra-226 at concentrations typically around 10 dpm/liter but may be as high as 40 dpm/liter (Holtzman 1964). Lakes which receive direct groundwater inflow would, therefore, tend to support large standing crops of Rn-222 and Pb-210.

Radium-226 and Rn-222 analyses were conducted on samples collected from the water column of Crystal Lake to determine if production of Pb-210 *in situ* was significant compared to atmospheric deposition of unsupported

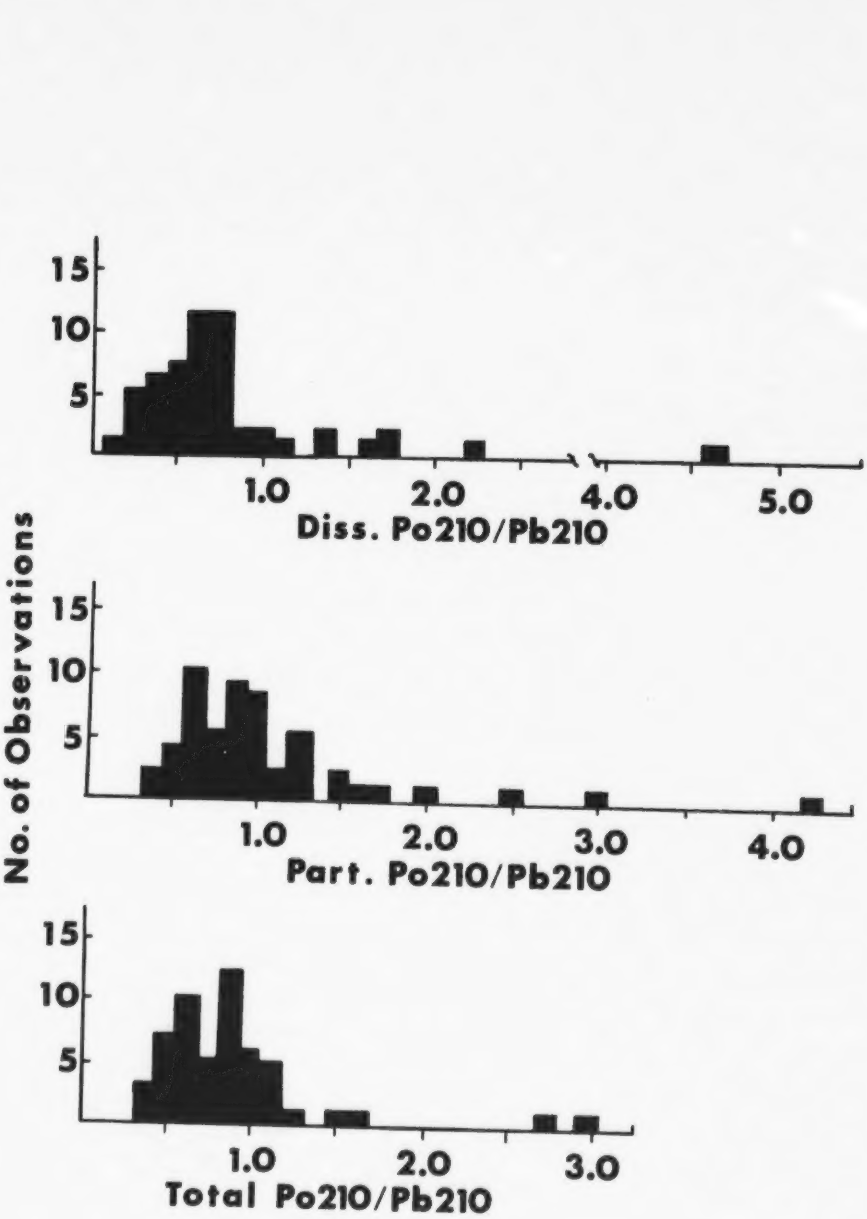


Figure 20. Frequency distributions of Po-210:Pb-210 activity ratios observed in Crystal Lake for all sampling dates (1979 to 80).

Pb-210. Water column profiles of Ra-226 and Rn-222 were obtained on three occasions during 1979 (6 June, 1 August, and 28 October). The average Ra-226 and Rn-222 concentration-depth profiles are shown in Figure 21. The data are presented as averages since the measured concentrations varied little between the three profiles. Total analysis error (Colman 1979) in the Ra-226 and Rn-222 concentrations is estimated to be ± 0.2 dpm/100 kg and ± 0.1 dpm/100 kg, respectively. All activities are corrected to the time of sample collection.

Radium-226 and Rn-222 concentrations in Crystal Lake are much lower than representative groundwater concentrations. Measured concentrations of Rn-222 were always in the range of 0.1 to 0.3 dpm/100 kg. Radium-226 concentrations were lower than Rn-222 activities and were just barely detectable, averaging 0.1 dpm/100 kg.

Colman (1979) found slightly higher concentrations of Rn-222 in Crystal Lake. His measurements of Rn-222 were made on samples collected ~ 1 m above the sediments under ice-covered conditions. Slow mixing near the bottom under ice cover may have produced higher apparent concentrations than those measured under the more dynamic wind-mixed conditions of the present study.

Concentrations of Rn-222 were highest near the sediment-water interface. Very close to the interface (<1 m) a measurable gradient usually exists due to the flux of Rn-222 out of the sediments (Colman 1979). Key et al. (1979b) estimate that only 30 to 40% of the Rn-222 produced from decay of Ra-226 in ocean sediment (Gulf of Mexico and Caribbean Sea sediments) reaches the overlying water. This is partially due to the short half-life of Rn-222 (3.82 days) and to its low apparent diffusivity (about 5×10^{-6} cm^2/sec) in sediment (Key et al. 1979b). Thus a large portion of the Pb-210 produced from sediment Ra-226 decay is probably retained in the sediment (assuming no post-depositional migration).

The Rn-222 which reaches the overlying water produces water column activities that slightly exceed Ra-226 activities. Due to dilution effects and radioactive decay of Rn-222, excess Rn-222 was only detected in the 20-m samples. In the rest of the water column Ra-226 and Rn-222 activities were not significantly different within the analytical uncertainties.

The measured concentrations of Ra-226 and Rn-222 are small compared to concentrations of Pb-210 in the lake. Concentrations of Pb-210 are always higher than Ra-226 or Rn-222 activities by a minimum factor of 10. This suggests that the majority of the Pb-210 in the water column of Crystal Lake is unsupported. The principal source of Pb-210 to Crystal Lake is most likely the atmosphere. Schell (1974) found that the atmosphere was the primary source of Pb-210 to Lake Washington. Most of the unsupported Pb-210 observed in sediments of the Great Lakes also apparently originates from atmospheric deposition (Robbins and Edgington 1975).

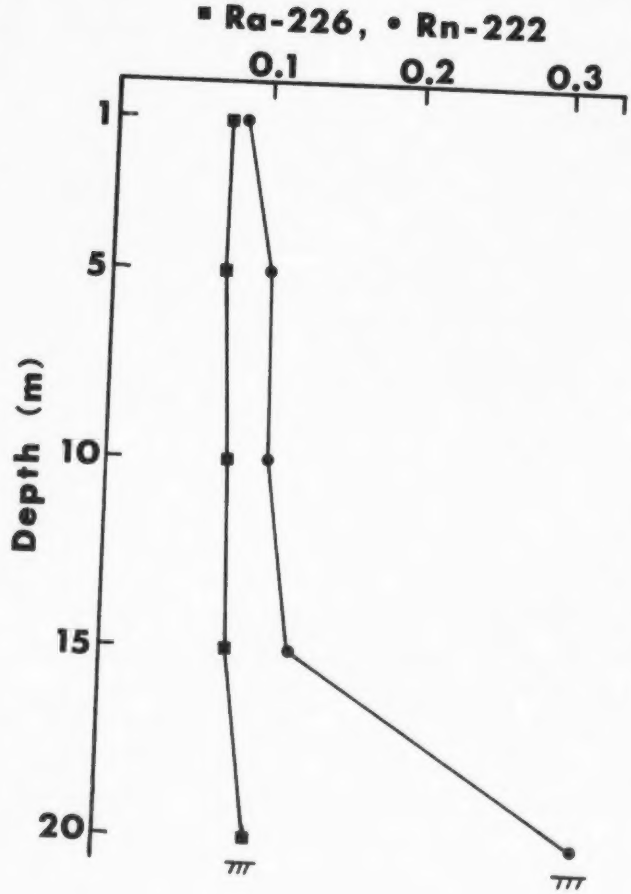


Figure 21. Average vertical profiles of Ra-226 and Rn-222 in Crystal Lake (dpm/100 kg).

CONCENTRATION OF Pb IN CRYSTAL LAKE

The average concentration of Pb in the surface water of Crystal Lake was 200 ng/kg on 27 October 1979. No distinction between dissolved or particulate phase was attempted. Since the samples were collected from a relatively unproductive period, the 200 ng/kg concentration of Pb is probably typical of steady-state conditions with respect to input and removal of Pb.

The concentration of Pb in Crystal Lake is presumably maintained by atmospheric input of anthropogenic Pb. If the average atmospheric flux of Pb is about 1.0 $\mu g/cm^2/yr$, the annual loading of Pb to Crystal Lake is approximately 3.1 kg. Using a total lake volume of 3.05×10^9 liters and a residence time of 1 yr for Pb in the lake, the Pb concentration should be around 1 μg/liter. This estimate is a factor of 5 greater than the measured Pb concentration of 0.2 μg/liter. The residence time of Pb in Crystal Lake is, therefore, much shorter than 1 yr.

An estimate of the residence time (τ) of Pb in Crystal Lake can be made as follows:

$$\tau_{Pb(yr)} = (C_w \cdot L)/I \qquad (2)$$

where:

C_w represents the mean total Pb concentration in the lake ($\mu g/cm^3$);

L is the average depth of the lake (cm); and

I is the annual mean atmospheric input of Pb to the lake ($\mu g/cm^2/yr$).

Substitution of numerical values into Eq. (2) gives a mean residence time of 0.2 yr for Pb in Crystal Lake. The mean residence time of Pb-210 in Crystal Lake also is about 0.2 yr (this study). The agreement in the estimates of the residence times of Pb and Pb-210 suggest that biological, chemical, and physical in-lake processes efficiently remove them from the water column. Schell (1974) found that Pb and Pb-210 have the same residence time in Lake Washington.

PLANKTON DATA

A summary of the experimental data for Pb, Pb-210, and Po-210 in plankton is shown in Table 5. The complete analytical data set is given in Appendix B. Net plankton (No. 25 mesh) was collected on three occasions during August. A subsample of the plankton was examined microscopically to identify the principal genera of phytoplankton and zooplankton.

All three surface samples (0 to 3 m) were composed almost entirely of phytoplankton. The dominant phytoplankter appeared to be *Dinobryon*, but green algae were also observed in large numbers. Baker (1974) found that *Dinobryon* composed 88% of the mid-summer phytoplankters in Crystal Lake

TABLE 5. WEIGHTED MEAN METAL CONCENTRATIONS (N = 9) AND PO-210:PB-210 ACTIVITY RATIOS IN PLANKTON (DRY WEIGHT). CONFIDENCE LIMITS WERE CALCULATED AT THE 95% LEVEL.

Plankton	Pb (mg/g)	Pb-210[a] (dpm/g)	Po-210[a] (dpm/g)	Concentration factor (X 10^{-4}) Pb[b]	Pb-210	Po-210	Po-210/Pb-210
Phytoplankton	0.28 ± 0.08	42.8 ± 33.9 (19.3 ± 15.3)	33.9 ± 10.0 (15.3 ± 4.5)	9.5	3.1	2.3	0.97 ± 0.57
Mixed zooplankton	0.08 ± 0.09	15.9 ± 10.7 (7.2 ± 4.8)	25.0 ± 6.5 (11.3 ± 2.9)	2.8	1.8	1.5	3.05 ± 2.44

[a] Values in parentheses are pCi/g.

[b] A water concentration of 200 ng/kg was used for calculating CF.

during 1973. Other phytoplankters of the genera *Cyanophyta* and *Chlorophyta* also were observed in this study and by Baker (1974).

Plankton samples obtained from the metalimnion and hypolimnion consisted primarily of zooplankters and are termed "mixed zooplankton" in Table 5. The principal zooplankters (estimate > 90%) were from the orders Eucopepoda (~ 50%) and Cladocera (~ 25%), subclass Ostracoda (~ 10%), and various genera of *Rotatoria* (~ 15%). Baker (1974) also identified these genera of zooplankton (except *Ostracoda*) as the principal summertime zooplankters in Crystal Lake.

Lead, Pb-210, and Po-210 concentrations were generally greater in phytoplankton than in zooplankton. These concentration differences, however, are barely significant at the $\alpha = 0.05$ level. The subsequent interpretation of the differences is, therefore, subjective. There are apparently no other measurements of Pb-210 or Po-210 reported for freshwater plankton.

The activity of Po-210 in marine plankton is similar to the levels observed in plankton collected in Crystal Lake. To deomonstrate this, a brief review of the data for marine plankton is presented. The literature data can be directly compared with that for Crystal Lake (Table 5) since they are both given on a dry weight basis.

Cherry (1964) measured Po-210 in a single sample of marine zooplankton and found about 38 dpm/g. Shannon and Cherry (1967) studied and measured the Po-210 activity in phytoplankton (6.2 dpm/g) and zooplankton (10.4 dpm/g). In a later study Shannon et al. (1970) coupled measurements of Po-210 with determination of the Pb-210 activity of various plankton. Their data indicated that Pb-210 activity was about 0.5 dpm/g in phytoplankton and zooplankton. As earlier studies indicated, Po-210 activity was greater in zooplankton (~ 6 dpm/g) than in phytoplankton (~ 2 dpm/g). Kharkar et al. (1976) also observed low Pb-210 activities in zooplankton (4.3 dpm/g) compared to Po-210 activities (~ 70 dpm/g).

The activity of Pb-210 and the concentration of Pb in Crystal Lake plankton are an order of magnitude greater than in marine plankton. Knauer and Martin (1973) observed Pb concentrations in marine phytoplankton ranging from < 1 to almost 40 μg/g (dry weight). Concentrations of Pb in Crystal Lake plankton ranged from 10 to 360 μg/g. The reason for higher concentrations in Crystal Lake plankton compared to marine plankton is not readily apparent. It is even more puzzling since the majority (> 90%) of the Pb-210 (and Pb?) in surface ocean water is in the dissolved phase (available?), whereas in Crystal Lake the majority of the Pb-210 is normally in the particulate phase (unavailable?). A more complete and detailed data base is needed for freshwater and marine environments to identify whether such a relationship exists.

The concentration factors (i.e., ratio of concentration in biota on a wet weight basis to that in water) for Pb, Pb-210, and Po-210 in Crystal Lake plankton are of the order of 10^4. The concentration factors of Pb, Pb-210, and Po-210 appear to be a factor of 2 or 3 greater in phytoplankton than in zooplankton. Holm (1978) observed concentration factors of 10^4 to 10^5 for Cd, Cu, and Zn in mixed freshwater plankton collected from six southern California lakes. Typical concentration factors of Po-210 in marine organisms are 10^3 to 10^4 (Shannon and Cherry 1967). Lead-210 generally exhibits a much lower concentration factor, around 10 to 10^3. These data suggest that freshwater plankton may concentrate some metals to a greater degree than their marine counterparts. Furthermore, the fact that concentrations are apparently higher in freshwater phytoplankton than in zooplankton suggests that these metals may not move as effectively through the food chain in freshwater systems as they apparently do in the marine environment.

Another interesting comparison between marine and freshwater plankton can be made by exmaining the activity ratio of Po-210:Pb-210 in phytoplankton and zooplankton. Kharkar et al. (1976) observed a mean activity ratio Po-210:Pb-210 of 16 for zooplankton collected in Caribbean Sea surface water. Shannon et al. (1970) found a similar ratio (14.1) in zooplankton collected off the Cape of Good Hope (South America). These data suggest that marine zooplankton have an activity ratio Po-210:Pb-210 of about 15. Shannon et al. (1970) determined that phytoplankton had a lower activity ratio than zooplankton. They estimated a mean ratio of 3.8 for phtoplankton; the ratio, however, was only based on three samples of phytoplankton. These results indicate that the activity ratio Po-210:Pb-210 might be four times greater in zooplankton than in phytoplankton. An analogous, but weak, relationship was observed in Crystal Lake plankton. The activity ratio in Crystal Lake zooplankton was about three times greater than in phytoplankton. This suggests than even though the activities of Pb-210 and Po-210 are apparently greater in freshwater plankton than in marine plankton, Po-210 may be preferentially concentrated by zooplankton in both systems. This hypothesis may explain some of the Po-210/Pb-210 disequilibrium observed in the ocean and in Crystal Lake.

RESULTS OF THE SEDIMENT TRAP EXPERIMENT

The results of the sediemnt trap study conducted in Crystal Lake from July through October 1979 are presented in Table 6. Based on all the trap collections, the mean mass deposition in the lake is 11.9 ± 2.9 mg/cm^2/yr (± 95% confidence limit). The majority of this material appears to be autochthonous biogenic material.

The mean fluxes observed during the stratified and unstratified periods are compared in Table 7. The mean elemental fluxes of Al, Pb Pb-210, and Po-210 were greater during the productive stratified period than after fall turnover. These differences are significant at the $\alpha = 0.05$ level.

The deposition of Po-210 decreased by a factor of 10 or more after fall turnover. The greatly accelerated deposition during the stratified period is attributed to the preferential removal of Po-210 by activities of the biosphere. This also is apparently the case for Po-210 in the ocean (Shannon et al. 1970, Turekian et al. 1974).

TABLE 6. ESTIMATED FLUXES FROM SEDIMENT TRAP EXPERIMENTS

Collection period (1979)	Depth[a] (m)	Mass (mg/cm^2/yr)	Al (µg/cm^2/yr)	Al (µg/cm^2)	Pb (µg/cm^2/yr)	Pb (µg/cm^2)	Pb-210 (dpm/cm^2/yr)	Pb-210 (dpm/cm^2)	Po-210 (dpm/cm^2/yr)	Po-210 (dpm/cm^2)
31 July to 31 Aug.	10.5	14.1	12	1	2.9	247	2.13	0.18	1.10	0.09
31 July to 31 Aug.	5.5	NA	NA	NA	NA	NA	NA	NA	NA	NA
31 July to 31 Aug.	2.5	17.0	12	1	1.9	160	1.91	0.16	0.80	0.23
1 to 9 Sept.	10.5	9.9	11	0.6	1.5	86	2.46	0.13	1.22	0.20
1 to 9 Sept.	5.5	13.3	8	0.4	3.0	555	1.94	0.11	0.98	0.16
1 to 9 Sept.	2.5	16.9	14	0.8	4.1	222	2.96	0.16	0.58	0.19
21 Sept. to 26 Oct.	10.5	5.0	6	0.5	0.9	86	0.82	0.08	ND	ND
21 Sept. to 26 Oct.	5.5	8.2	9	0.9	1.1	111	1.11	0.11	0.12	0.01
21 Sept. to 26 Oct.	2.5	11.1	10	0.9	1.6	160	1.51	0.14	ND	ND
MEAN		11.9	10	0.8	2.1	203	1.86	0.13	0.80	0.14

[a] Depth above sediment.

NA – Not available, material lost from trap during recovery.

ND – Not detected.

TABLE 7. COMPARISON OF MEAN FLUXES IN CRYSTAL LAKE DURING STRATIFIED AND UNSTRATIFIED PERIODS. CONFIDENCE LIMITS FOR THE MEAN WERE CALCULATED AT THE 95% LEVEL

Interval	Mean				
	Mass	Al	Pb	Pb-210	Po-210
Stratified	14.2 ± 2.6	11 ± 2	2.7 ± 0.9	2.28 ± 0.39	0.94 ± 0.22
Unstratified	8.1 ± 3.5	8 ± 2	1.2 ± 0.4	1.15 ± 0.39	< 0.1

[a] Units are for mass ($mg/cm^2/yr$), Al and Pb ($\mu g/cm^2/yr$), Pb-210 and Po-210 ($dpm/cm^2/yr$).

Deposition of Pb and Pb-210 was approximately twice as fast during the stratified period as in the less productive fall period. The analogous behavior of Pb and Pb-210 suggests that similar mechanisms remove them from the water column.

In contrast to the more reactive trace metals, Al deposition only increased moderately (27%) during the productive summer season. The increased deposition of Al may be in response to more efficient particle removal processes operating in the stratified period. Aggregation of particles, resulting in increased settling velocities (McCave 1975), is probably more common when detritus and other biogenic debris are plentiful. Small particles may be aggregated to form large, rapidly settling particles by physiochemical processes or by biological ingestion and conversion into their by-products, such as fecal pellets. The incorporation of minerals into fecal pellets may account for their rapid settling and low residence time in the ocean (Krishnaswami and Sarin 1976).

During the stratified period the mass flux was almost twice as much as it was after fall turnover. This increased deposition of material during the stratified period is ascribed to biologically mediated particle production processes. The association of trace elements with such particulate matter most likely accounts for their low residence times in Crystal Lake.

SECTION 8

ESTIMATES OF ATMOSPHERIC DEPOSITION

INTRODUCTION

The atmosphere is probably the major route for material transport to Crystal Lake. Consequently, a portion of the research focused on obtaining experimental data from which atmospheric deposition could be estimated. This section presents estimates of wet and dry atmospheric fallout of Al, Pb, Pb-210, and Po-210.

WET DEPOSITION

Wet deposition of Pb, Pb-210, and Po-210 was measured directly by analyzing rainfall. The measured concentrations can be expressed as wet fluxes when the area of the collection funnel and the sampling time interval are known. The estimates of wet deposition of Pb, Pb-210, and Po-210 calculated in this manner are presented in Table 8. Note that the fluxes vary by more than a factor of 5.

For the summer of 1979 the mean wet fluxes of Pb and Pb-210 were 0.8 $\mu g/cm^2/yr$ and 1.58 $dpm/cm^2/yr$, respectively. Wet deposition also can be estimated using the weighted mean concentration in rain and the annual average rainfall (80 ± 15 cm). The weighted mean concentration of Pb in rain was 7.9 μg/kg and 17.4 dpm/kg for Pb-210. The annual wet flux of Pb computed using these data is 0.6 ± 0.1 $\mu g/cm^2/yr$. Similarly, we obtain 1.4 ± 0.3 $dpm/cm^2/yr$ for Pb-210.

The two methods of estimating wet deposition of Pb and Pb-210 yield essentially the same values for the mean fluxes. Since the summer of 1979 was abnormally dry, the measured mean fluxes of 0.8 $\mu g/cm^2/yr$ for Pb and 1.58 $dpm/cm^2/yr$ for Pb-210 probably provide the best estimate of the 1979 wet fluxes. The nature of the errors involved and the limited data makes a more rigorous estimate of the wet fluxes impossible. In general, year-to-year average wet fluxes are probably best estimated using weighted mean concentrations.

Since Po-210 was only detected in rainfall on three occasions, an estimate of its wet deposition is uncertain. The weighted mean concentration of Po-210 in rain was 1.3 dpm/kg. This concentration gives an annual mean flux of 0.1 $dpm/cm^2/yr$. Hence, the wet flux of Po-210 is <10% that of

TABLE 8. WET DEPOSITION ESTIMATES

Time interval	Pb		Pb-210		Po-210	
(1979)	(ng/cm^2)	($\mu g/cm^2/yr$)	(dpm/cm^2)	($dpm/cm^2/yr$)	(dpm/cm^2)	($dpm/cm^2/yr$)
4 to 22 June	48	1.0	0.13	2.63	0.02	0.35
23 June to 10 July	13	0.3	0.05	0.92	-	-
11 to 30 July	23	0.4	0.12	2.29	-	-
31 July to 15 Aug.	92	2.2	0.10	2.40	-	-
16 Aug. to 2 Sept.	16	0.3	0.03	0.73	0.001	0.01
3 to 21 Sept.	18	0.4	0.03	0.53	0.001	0.03
Mean ± 95% C.I.	35 ± 25	0.8 ± 0.6	0.08 ± 0.04	1.58 ± 0.76	<0.01	<0.1

Pb-210. Poet et al. (1972) observed this same relationship between fluxes of Pb-210 and Po-210 at Boulder, Colorado.

The nature of the analytical scheme employed made it impossible to directly measure wet deposition of Al. Wet deposition of Al can be predicted, however, using an empirical relationship known as the washout ratio (W). The washout ratio relates the concentration of a substance in unwashed air to its concentration in rain. The washout ratio (Chamberlain 1960, Slinn 1977) is defined as:

$$W = \rho_a K/X \qquad (3)$$

where:

K = the concentration of a substance in rain
X = its concentration in unwashed air
ρ_a = the density of air (1200 g/m^3).

Ideally, it is desirable to know X and W at cloud base, but the empirical relationship of Eq. (3) can be used to estimate values of K near the ground if X and W also are measured at ground level. Wet deposition is derived from Eq. (3) by multiplying K by the rainfall.

The mean concentration of Al in air was 233 ng/m^3 from May to October 1979. (See Appendix B) Using the measured MMD of 1.7 μm for Al, a value of 230 is obtained for W from the empirical data of washout ratio versus particle diameter (Gatz 1975). The predicted mean concentration of Al in rain is 44.6 μg/liter. The annual mean wet deposition of Al is thus estimated to be 3.6 $\mu g/cm^2/yr$.

The washout ratios of Pb and Pb-210 can be calculated using Eq. (3). Values of W shown in Table 9 were calculated using mean air and rain concentrations for each of the indicated sampling intervals. The overall mean value of W for Pb-210 is 1088, about two-fold higher than the value of W for Pb (511). For the 31 July to 15 August period the mean value of W was 1500 for Pb and Pb-210. The mean value of W for Pb is 300 and 1000 for Pb-210 when this sampling period is excluded. These values of W indicate that, on the average, W is about three times higher for Pb-210 than for Pb. This relationship is also evident in the mean values of the specific activity (dpm/mg) of Pb-210:Pb in rain and aerosol (Table 9). The mean specific activity of rain is 2705, or roughly, three times the specific activity of air (831).

The reason for the higher values of W for Pb-210 relative to values of W for Pb is not readily apparent for the available data. Based on the relationship between W and particle diameter presented by Gatz (1975) and the observed MMDs of 0.40 μm for Pb-210 and 0.55 μm for Pb, Pb-210 and Pb should be washed from air with approximately the same efficiency. In addition, the theoretical collision efficiency of aerosol particles with raindrops is not significantly different for 0.40 and 0.55 μm particles (Slinn 1977).

TABLE 9. WASHOUT FACTORS AND SPECIFIC ACTIVITIES

Time interval (1979)	W		Rain	Air
	Pb	Pb-210	(dpm/mg)[a]	(dpm/mg)[a]
4 to 22 June	280	1192	2720	654
23 June to 10 July	282	1182	3574	843
11 to 30 July	189	1344	5261	731
31 July to 15 Aug.	1584	1490	1069	1027
16 Aug. to 2 Sept.	190	489	2122	738
3 to 21 Sept.	542	829	1483	990
Mean	511	1088	2705	831

[a] Pb-210:Pb.

A possible explanation for the "apparently" scavenging efficiency of rain for Pb-210 compared to Pb may be as follows. Radon-222, the precursor of Pb-210, emanates from the earth's surface at a fairly constant rate and penetrates the entire troposphere and into the stratosphere before decaying to Pb-210 (Moore et al. 1973). This dispersion of Rn-222 provides a reasonable constant and homogeneous production of Pb-210 in the lower troposphere. Thus, the value of the washout ratio for Pb-210 is probably more or less constant as a function of altitude in the lower troposphere.

Stable Pb, on the other hand, is injected into the atmosphere close to the earth's surface where vertical mixing does not provide a uniform airborne concentration. The airborne concentration of stable Pb is, therefore, most likely higher near the ground than at cloud base. Hence, the average value of the washout ratio observed for Pb in the present study may be low due to biased ground level air concentrations of Pb used in the calculations. If the airborne concentration of Pb was determined as a function of altitude so a more representative concentration was obtained, the values of the washout ratio for Pb and Pb-210 might be similar. A vertical tropospheric profile of Pb-210/Pb in air and rain might yield information about aerosol-rain interactions.

The source function of stable Pb in the atmosphere varies--spatially and temporally--by orders of magnitude. However, the airborne concentration of Pb-210 is uniform compared to aerosol Pb concentrations over continental land surfaces (Turekian et al. 1977). These factors suggest that values of W for stable Pb probably vary more than values of W for Pb-210 at a particular site. The differential variability in the values of W for Pb and Pb-210 is evident in the present data (Table 9), where W for Pb varies by a factor of 8, compared to a factor of 3 for Pb-210.

DRY DEPOSITION: THE MODELING APPROACH

Although the direct measurement of material deposition in rainfall is straightforward, dry particle deposition is difficult to quantitate even if air concentrations are accurate and representative. Since mass transfer from atmosphere to water depends on meteorological conditions (Sehmel 1980), atmospheric sampling must have sufficient time resolution to coincide with changing meteorological conditions. This often means sampling times are required which are too short to provide accurate atmospheric concentrations. A trade-off is usually made in that time-integrated atmospheric sampling is combined with as much appropriate meteorological information as possible. Even if accurate data are obtained, present estimates of dry deposition for many substances are probably only accurate within an order of magnitude (Andren and Strand 1981).

The mechanisms for removal of particles from the atmosphere include gravitational settling, impaction, and electrostatic effects (Sehmel and Sutter 1974). Experimental evidence has shown that the rate of particle deposition is critically dependent on wind speed (Sehmel and Sutter 1974). This suggests that particle deposition cannot be satisfactorily described by simple gravitational settling. From consideration of momentum transfer at the air-water boundary, it has become apparent that particle deposition to water surfaces has to be parameterized to include meteorological and surface determined variables.

Sehmel and Hodgson (1974) proposed a two compartment particle deposition model where mass (particle) transfer processes are described by micrometeorological eddy diffusivities and Brownian diffusion. Predictions using their model indicate that the rate of particle deposition increases as aerodynamic surface roughness height increases, usually as friction velocity increases, and the rates are almost independent of atmospheric stability. Different approaches have recently been proposed (Hicks and Williams 1980, Slinn and Slinn 1981) to describe aerosol deposition to water, but there are still discrepancies between model predictions and field measurements. The model used in this research to estimate particle deposition was the mass transfer approach proposed by Sehmel and Hodgson (1974) because the required support data was available. Andren and Strand (1981) have recently used the model of Sehmel and Hodgson (1974) to estimate deposition of total organic C to Lake Michigan.

The dry particle flux to the water surface is described by a one-dimensional, steady-state continuity equation:

$$F = -(\varepsilon + D)\frac{dC}{dz} - V_t C \qquad (4)$$

where:

F = the particle flux (g/cm^2/sec)

ε = the particle eddy diffusitity in air (cm^2/sec)

D = the Brownian diffusivity in air (cm^2/sec)

z = the height (cm) above the water surface at which the particle concentration C (g/cm^3) is measured

V_t = the particle terminal settling velocity.

The model assumes that particle agglomeration does not occur during deposition and that particles are completely retained by the water surface (i.e., the water acts as a perfect particle sink).

The relationship between particle flux and air concentration and the deposition velocity V, can be obtained from an integrated form of Eq. (4):

$$V_z = \frac{V_t}{1 - (1/\alpha)}. \tag{5}$$

The deposition velocity is defined in Eq. (5) in terms of the air concentration reference height z. Equation (5) shows that the lower limit of a predicted deposition velocity is the gravitational settling velocity.

In Eq. (5) α is given by:

$$\alpha = \exp\,(-V_t\ \mathrm{Int}/U_*) \tag{6}$$

where:

U_* = the friction velocity (cm/sec) and Int represents a dimensionless diffusional resistance based on dimensionless expressions of eddy and Brownian diffusivity.

Thus, as diffusional resistance becomes less, Eq. (5) predicts that the deposition velocity increases beyond the gravitational settling velocity.

The resistance integral Int represents turbulent and surface resistances to mass transfer. Int was divided into Int_1 (aerodynamic resistance) and Int_2 (surface resistance) so that the resistances could be evaluated independently:

$$\mathrm{Int} = \mathrm{Int}_1 + \mathrm{Int}_2 = - U_* \int_{z_{C_z}}^{z_{1\mathrm{cm}}} \left(\frac{dz}{\varepsilon} - \mathrm{Int}_2\right) \tag{7}$$

The surface resistance Int_2 (0 to 1 cm height) has been evaluated by Sehmel and Hodgson (1974) from wind tunnel determined deposition velocities by a dimensionless correlation:

$$\begin{aligned} \mathrm{Int}_2 = - \exp \Bigg\{ &- 23.667 + 5.555 \ln \frac{d}{z_o} \\ &- 0.07681 \left(\ln \frac{d}{z_0}\right)^2 + 0.9722 \ln \frac{U_*}{V_t} \\ &+ 0.03799 \left(\ln \frac{U_*}{V_t}\right)^2 - 2.254 \ln \frac{D}{U_* z_0} \\ &- 3.724 \ln \frac{\rho U_* d^2}{18 \mu z_0} \Bigg\} \end{aligned} \tag{8}$$

where:

d = particle diameter (cm)

z_0 = the surface roughness height (cm)

ρ = particle density (1.5 g/cm^3), and

μ = air viscosity.

Values of U_* to be used in Eqs. (6 and 8) may be obtained from measurements of mean wind speed ($\bar{U}_{10}$) at a height of 10 m (Wu 1969):

$$U_* = 7.1 \times 10^{-3} \cdot \bar{U}_{10}^{1.25} \tag{9}$$

Predicted deposition velocities are shown graphically in Figures 22 and 23 for typical roughness heights and values of 25 and 55 cm/sec for U_*. Only in the particle diameter range from about 0.1 to 1 μm is the deposition velocity constant for a selected surface roughness and friction velocity.

Dry Deposition: The Computational Procedure

Four different wind speeds were chosen arbitrarily to represent typical values of U_* over the whole year. These wind speeds were: <5 m/sec (40% of the year), 5 to 10 m/sec (40% of the year), 10 to 15 m/sec (15% of the year), and >15 m/sec (5% of the year). The cumulative frequency of wind speed occurrence was taken from the data of Sievering et al. (1979) for Lake Michigan. A statistical evaluation of the wind frequency distribution is not available for Vilas County, Wisconsin. The error introduced in the final flux estimates from using the Lake Michigan wind data is probably small compared to other model uncertainties.

Airborne concentrations of Al, Pb, Pb-210, and Po-210 were averaged to obtain mean values for the air concentration as a function of particle diameter (impactor stage). Air concentrations were averaged for two periods: 1. the warm season, when there was open water on the lake (May to mid-November), and 2. the cold season, when the lake was snow and ice covered (mid-November to late April). The mean air concentrations of Al, Pb, Pb-210, and Po-210 are shown as a function of particle diameter in Figures 24 and 25 for the warm and cold seasons, respectively.

In calculating the particle deposition velocities for the warm season, roughness heights were calculated from the relationship for water surfaces proposed by Wesely et al. (1978):

$$z_0 = \frac{0.016 U_*^2}{g} + \frac{\mu}{9.1 U_*} \qquad (10)$$

where:

g = the acceleration due to gravity (cm/sec^2)
μ = the kinematic viscosity of air (g/cm/sec).

Values of z_0 were 0.005, 0.015, 0.05, and 0.11 (cm) for $U_* = 17$, 30, 55, and 83 cm/sec, respectively. Roughness heights between 0.001 and 0.01 cm were assumed for conditions when the lake was snow and ice covered (Sehmel, 1980).

Particulate elemental fluxes were estimated for the warm and cold seasons as follows. Using the elemental mass versus particle diameter information presented in Figures 24 and 25, particle deposition velocities

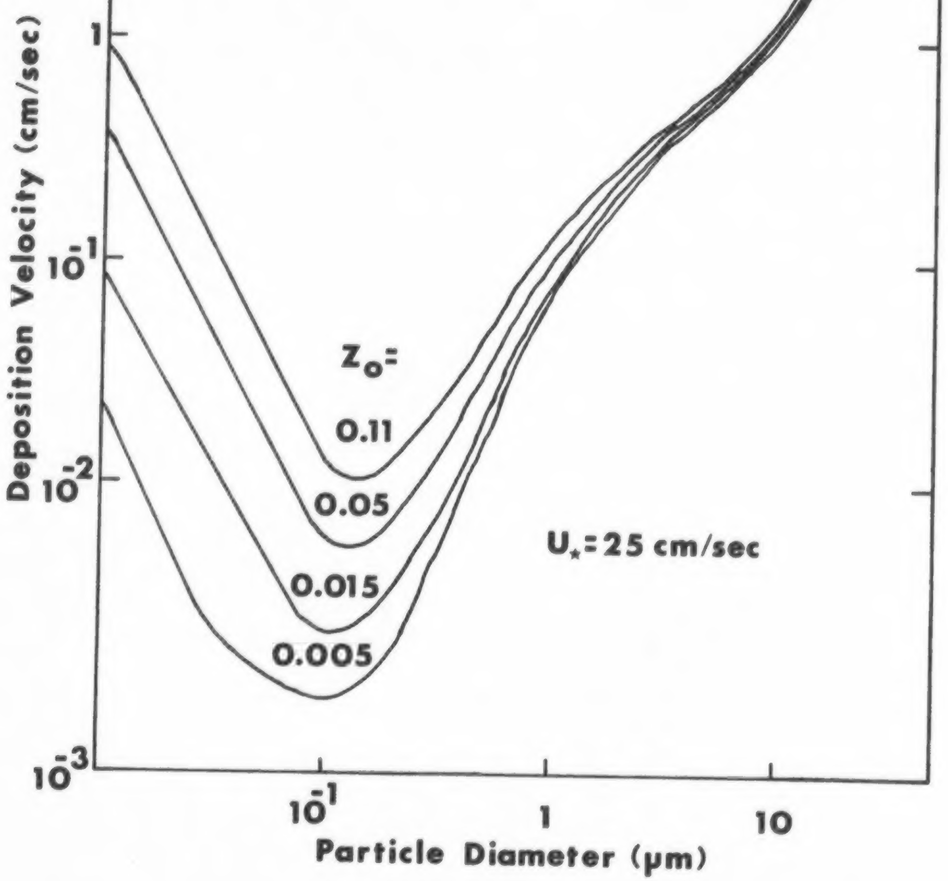


Figure 22. Predicted deposition velocities at z=5 m as a function of particle diameter for $U_* = 25$ cm/sec and selected values of z_0 (cm).

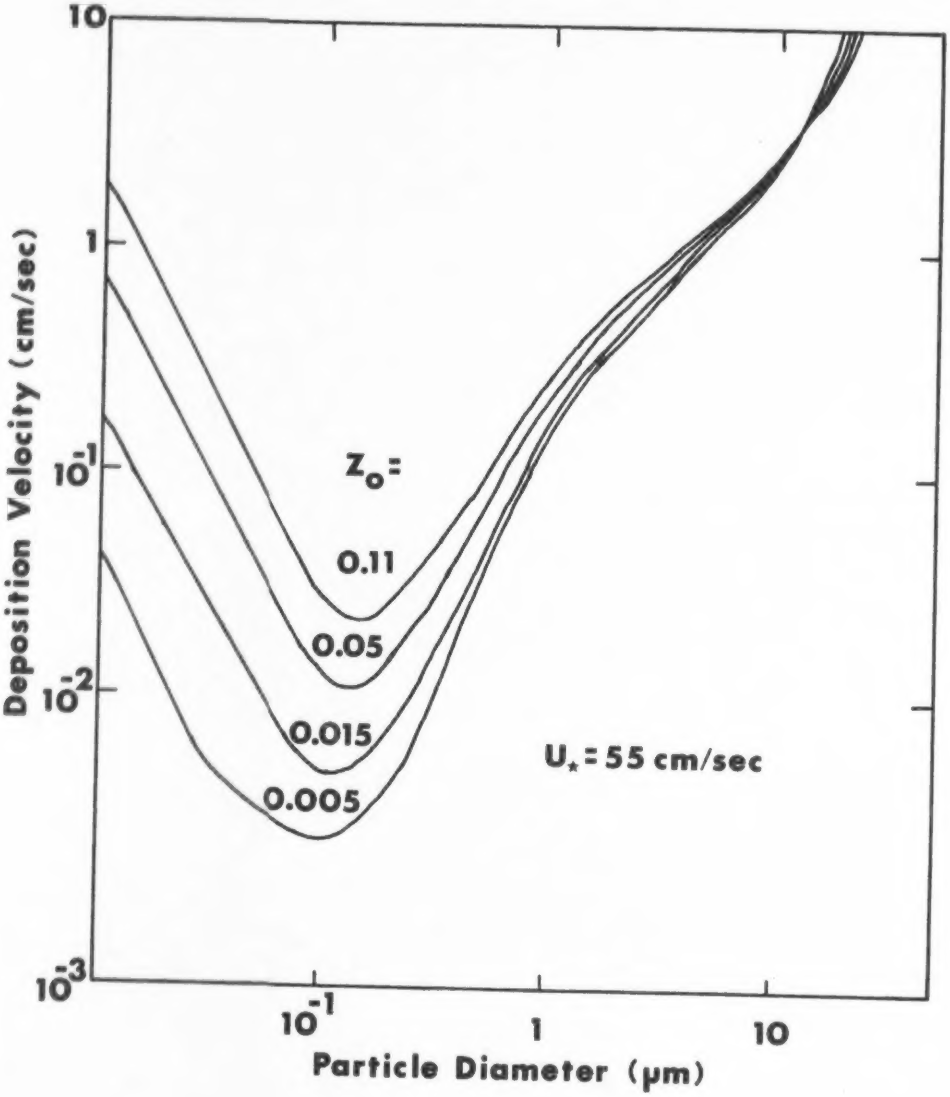


Figure 23. Predicted deposition velocities at z=5 m as a function of particle diameter for $U_* = 55$ cm/sec and selected values of z_0 (cm).

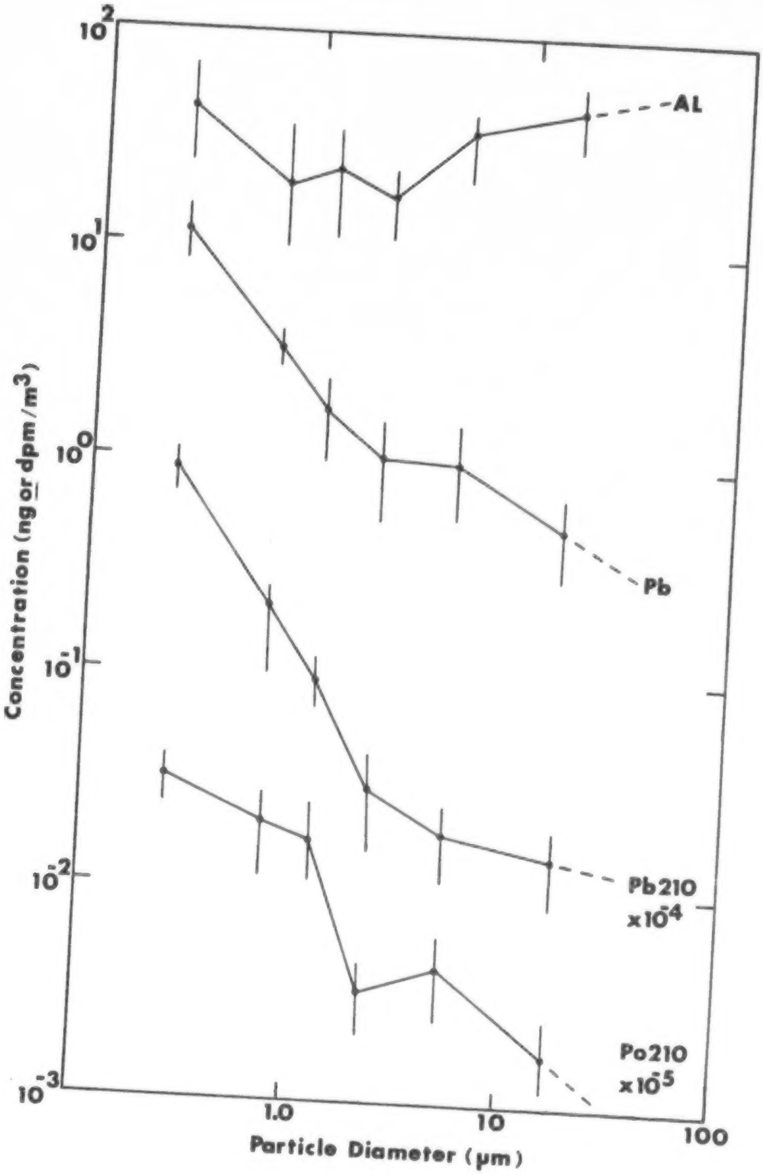


Figure 24. Average atmospheric concentrations (n=4) during the warm season as a function of particle diameter.

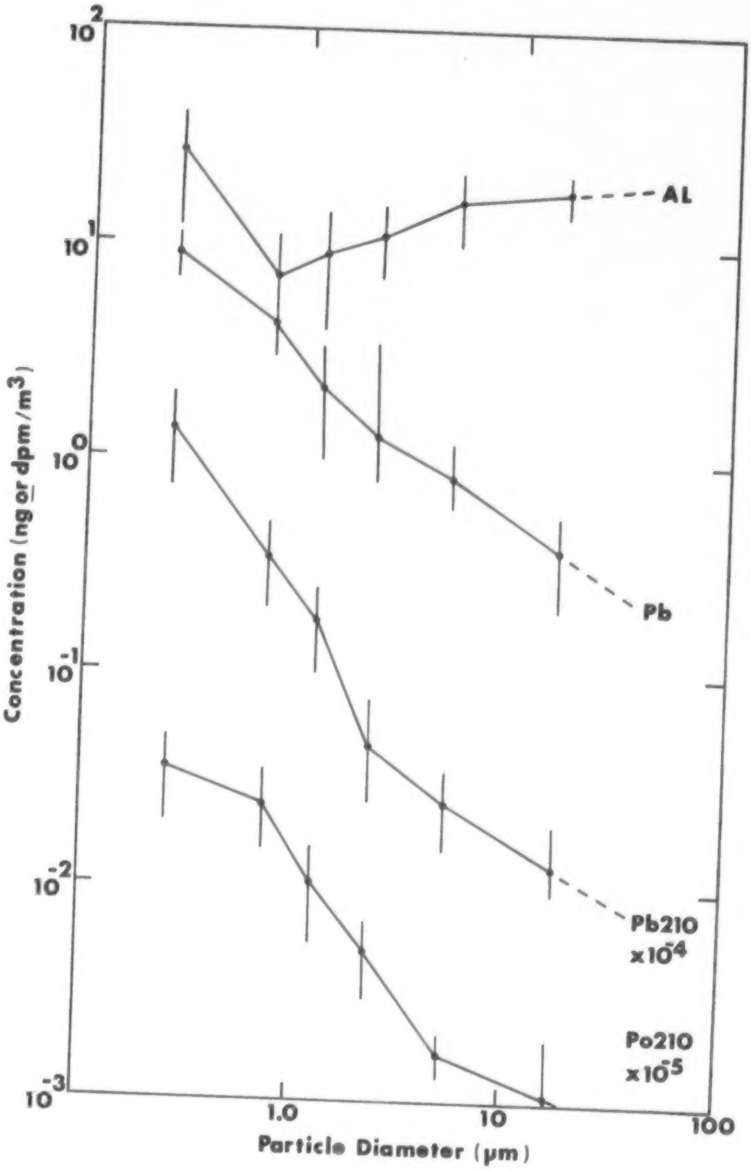


Figure 25. Average atmospheric concentrations (n=4) during the cold season as a function of particle diameter.

determined by the method of Sehmel and Hodgson (1974) were weighted according to the area under the curve for the appropriate range of particle diameters (impactor stage). The per-stage elemental fluxes were subsequently computed for specified ranges of particle diameter by multiplying an overall weighted deposition velocity by the corresponding elemental mass. The per-stage fluxes were summed to obtain a total elemental particle flux. The details of the computational procedure follow.

Graphical integration (Figures 24 and 25) was used to determine the weighting factor for deposition velocities of particle diameters > ≃ 1 μm (i.e., stages 1, 2, and 3). For the spectrum of particles > 1 μm, deposition velocities vary at least 100-fold. The upper particle diameter considered in the present calculations was 40 μm. Davidson (1977) found that particles larger than 40 μm are collected occasionally by cascade impactors, but the number of these particles is usually too small to be statistically significant.

At a sampling rate of 1.1 m^3/min the particle ranges collected by the impactor stages were assumed to be: stage 1, 7.2 to 40 μm; stage 2, 3.0 to 7.2 μm; and stage 3, 1.5 to 3.0 μm. These size ranges correspond to theoretical particle collection efficiencies. The actual particle size distributions collected by each stage during the present study are unknown. It was beyond the scope of this research to examine discrepancies between theoretical and field particle collection efficiencies. Suffice it to say that large uncertainties may be introduced by assuming theoretical particle collection efficiencies (Sievering et al. 1978).

The average elemental mass collected by each of the impactor stages has been plotted at the mid-point of the particle diameter range in Figures 24 and 25. Thus around each mid-point lies the theoretical range of particle diameters collected by that particular stage. Each range of particle diameters was divided into five equal subdivisions. The average deposition velocity was estimated using the method of Sehmel and Hodgson (1974) for each particle diameter subdivision. The weighting factor determined from the appropriate fractional area under the curve (Figures 24 and 25) was used to adjust the deposition velocity for the measured elemental mass-particle diameter distribution.

For stages 1, 2, and 3 an overall average deposition velocity was calculated for each stage by summing the products of the deposition velocity and weighting factor for the five particle diameter subdivisions. To calculate the mean per-stage elemental flux the overall average deposition velocity was multiplied by the stage's measured elemental mass. The per-stage elemental fluxes were summed to obtain an estimate of the flux attributed to stages 1 through 3.

Since deposition velocity is nearly constant for particle diameters between ~ 0.1 and 1 μm, deposition velocities for stages 4, 5, and the backup were determined for the aerodynamic particle diameters corresponding to the theoretical 50% collection efficiencies. The per-stage fluxes were calculated as before.

The total particulate elemental flux was determined by summing all the per-stage fluxes. The computational procedure was repeated using the different deposition velocities calculated for each of the four wind speed ranges. The average particulate elemental fluxes were determined for the warm and cold seasons for the total fluxes calculated for each wind speed range. The fluxes at each wind speed range were weighted using the cumulative frequency of wind speed occurrence.

Dry Deposition: The Model Estimates

The estimates of dry deposition made with the previously described computational procedure are presented in Table 10. Dry particle fluxes of Pb and Pb-210 tended to be slightly higher during the cold season compared to the warm season. Owing to model uncertainties it is probably best to consider them to be equal at the present time. Thus, the annual mean dry deposition flux of Pb is 0.2 μg/cm^2/yr and 0.21 dpm/cm^2/yr for Pb-210. The particulate flux of Po-210 appears to be 0.01 dpm/cm^2/yr.

TABLE 10. AVERAGE DRY DEPOSITION ESTIMATES

Element	Deposition flux[a] Warm season	Deposition flux[a] Cold season
Al	7.9	5.9
Pb	0.15	0.25
Pb-210	0.19	0.23
Po-210	0.014	0.006

[a] Units are: μg/cm^2/yr for Al and Pb, dpm/cm^2/yr for Pb-210 and Po-210.

The dry particle flux of Al appears to be less during the cold season. Such a result might be expected since the air concentration of Al averaged 233 ng/m^3 during the warm season compared to 131 ng/m^3 during the cold season. The lower wintertime atmospheric Al concentrations may reflect the loss of the local resuspended component from the airborne particle distribution while the ground was snow covered. The ground is usually covered with snow for at least 120 days/yr at this site.

The model calculations indicate that most of the dry flux is carried by particles > 1 μm. Since a large percentage of the particles > 1 μm have deposition velocities of the order of several cm/sec, it is critically important to quantify the large particle elemental flux. Unfortunately uncertainties exist in the present dry deposition estimates due to the fact that the true upper particle diameter cutoff collected by the air sampler is unknown. Furthermore, the elemental mass associated with a given range of particle diameters is not known precisely. As more is learned about particle deposition to surfaces in general, the present dry deposition estimates can be revised.

Dry deposition experiments were conducted during July and August. These experiments were performed to obtain a few field measurements of dry deposition of Pb and Pb-210. Dry deposition was collected on a horizontal sheet of Whatman 41 filter paper sheltered beneath a plastic cover. The results of three 19-day experiments are summarized below:

	Dry Flux		V_d
Pb	23 ng/cm^2	0.2 µg/cm^2/yr	0.29 cm/sec
Pb-210	0.002 dpm/cm^2	0.15 dpm/cm^2/yr	0.23 cm/sec

These fluxes agree surprisingly well with those estimated using the model of Sehmel and Hodgson (1974) and the airborne concentrations of Pb and Pb-210.

The time averaged deposition velocities, $\bar{V}_d$, for Pb and Pb-210 were calculated (Chamberlain 1960):

$$\bar{V}_d = \frac{-F}{C} \tag{11}$$

where:

$\bar{V}_d$ = time averaged deposition velocity (cm/sec)

F = the flux (downward)

C = the airborne concentration.

In calculating $\bar{V}_d$ the mean monthly air concentrations (i.e., July and August) of Pb and Pb-210 were used.

Davidson (1977) and Nriagu (1978) have summarized dry deposition velocities for Pb particulates at several locations worldwide. A value of 0.3 cm/sec is a reasonable estimate for these data which is in agreement with the value of 0.29 cm/sec observed in the present study. The observed agreement in the deposition velocities of Pb and Pb-210 indicates that dry particle deposition dynamics of Pb and Pb-210 are similar for non-urban locations.

ATMOSPHERIC DEPOSITION DETERMINED FROM SNOW CORES

Elemental deposition was estimated for Pb, Pb-210, and Po-210 from cores of snow collected at the atmospheric monitoring site (cores 1 to 3) and atop the ice on Crystal Lake (cores 4 to 6). The deposition estimates are presented in Table 11. The results for cores 1 to 6 are considered to represent total (wet plus dry) atmospheric fallout. Deposition in fresh snowfall is represented by the values for cores 7 and 8. Fresh snowfall was collected from a previously bare area of ice on Crystal Lake (mid-lake site) after an overnight snowfall of ~ 12 cm under calm wind conditions.

TABLE 11. ATMOSPHERIC DEPOSITION ESTIMATED FROM SNOW CORES

Core No.	Pb (ng/cm^2)	Pb-210 (dpm/cm^2)	Po-210 (dpm/cm^2)
1	106	0.09	0.01
2	65	0.07	0.02
3	42	0.08	0.02
4	52	0.08	0.02
5	49	0.06	0.02
6	59	0.13	0.05
Mean ± 95% C.I.	62 ± 18	0.09 ± 0.03	0.02 ± 0.01
7[a]	33	0.05	0.02
8[a]	28	0.03	0.01

[a] Fresh snowfall.

The total deposition estimates presented in Table 11 must be considered as approximate values since the snow was subjected to melting and high wind conditions. Seip (1980) has shown that concentrations of elements in snow cores change dramatically, both up and down, over a period of hours to days. This is mainly due to freezing and thawing which preferentially mobilizes certain elements. For these reasons it is felt that it is not appropriate to calculate fluxes from these data.

The difference between the estimates of total atmospheric fallout and fresh snowfall (wet deposition) may be interpreted with caution as an indication of dry deposition. Compared to the dry deposition estimates observed in the summertime, dry deposition in the winter may contribute a larger percentage of the total atmospheric fallout.

ESTIMATES OF TOTAL ATMOSPHERIC FLUXES

The annual mean atmospheric fluxes of Al, Pb, Pb-210, and Po-210 are summarized in Table 12. Turekian et al. (1977) have found that several years data for atmospheric fallout of Pb-210 may fit the average flux to no better than 10 to 50%. The excellent agreement between atmospheric input and accumulation of Pb and Pb-210 in Crystal Lake sediments (Section 11) suggests that the data (Table 12) are fairly representative of year-to-year mean atmospheric fluxes of Pb and Pb-210 at this site. If the uncertainty in the sedimentation rate determined flux of Pb-210 is about 20% (Section 12), then the estimate of the atmospheric flux of Pb-210 probably has approximately the same degree of uncertainty. These data also indicate that the uncertainty in the atmospheric flux of Pb is about the same as that estimated for Pb-210.

TABLE 12. ESTIMATES OF TOTAL ATMOSPHERIC FLUXES

Element	Wet[a]	Dry	Total	Wet total	Units
Al	3.6	6.9	10.5	0.34	$\mu g/cm^2/yr$
Pb	0.8	0.2	1.0	0.80	$\mu g/cm^2/yr$
Pb-210	1.58	0.21	1.79	0.88	$dpm/cm^2/yr$
Po-210	<0.1	0.01	<0.1	<0.90	$dpm/cm^2/yr$

[a] Based on rain deposition only.

In general, the ratio of wet:total deposition of Pb-210 (0.8 to 0.9) is probably representative since Pb-210 is fairly uniformly distributed in the atmosphere. Thus, for regions with similar precipitation patterns these conditions probably depict atmospheric deposition of Pb-210 quite well.

For Pb, however, the same may not be true for all areas even if they have similar precipitation patterns. This is due to different source strengths, spatially and temporally. The wet:total ratio of 0.8 for Pb may be representative of reasonably remote temperate climates. Dry deposition fluxes of Pb may be considerably more important in urban areas, i.e., close to points of emission.

SECTION 9

DYNAMICS OF Pb-210 IN THE WATER COLUMN

DEVELOPMENT OF THE TWO-LAYER MODEL

Results obtained from the water samples show that dissolved and particulate concentrations of Pb-210 are subject to large spatial and temporal variations suggesting that non-steady-state processes strongly influence Pb-210 distribution. Thus, it seems unlikely that a simple examination of individual concentration-depth profiles will provide meaningful results. It is thought that a more informative approach would be to integrate the data over large enough layers of the water column to minimize localized nonsteady-state effects. In other words, a description of the net fluxes of Pb in the lake. Although this type of approach does not provide the details of the geochemical cycle of Pb, it should define which processes or events are most important. These processes can then be studied in greater detail. This type of information for trace metals is essentially nonexistent for lakes and is crucial for developing a generalized picture of geochemical cycles in lakes.

The approach taken here was to integrate the measured dissolved and particulate concentrations over the entire water column. This was accomplished by graphically connecting data points and interpolating to determine the concentration of 1 m intervals. The dpm of Pb-210 were calculated for each layer and summed to determine whole lake inventories of dissolved and particulate phases. The whole lake inventories of dissolved and particulate Pb-210 are shown in Table 13 for 10 profiles collected during 1979 to 1980.

To examine the spatial and temporal variation of Pb-210 in the water column, the lake was considered as a two-layer system. The lake was divided subsequently into a surface mixed layer (SML) and a deep layer (DL). The SML is considered to be a layer mixed by wind-induced turbulence. During thermally stratified periods this layer was defined as that water which was above the thermocline region where essentially isothermal conditions prevailed. The DL contained all water below the SML. When the lake was not stratified, the water column was divided in half with the SML being $\leq$ 10 m and the DL > 10 m. This division of the water column at 10 m was based on experimental evidence which suggested the lake was not well mixed with respect to certain constituents (e.g., particulates). If one examines the concentration-depth profiles (Figures 9 to 18), it is evident that 10 m appears to define a depth where concentrations of Pb-210 in dissolved and particulate phases are higher above than below.

TABLE 13. WHOLE LAKE INTEGRATED Pb-210 PROFILES (X 10^{-8} DPM)

Date	Dissolved	Particulate	Total
		1979	
5 June	1.09	3.67	4.77
23 June	0.89	5.02	5.91
11 July	0.60	2.27	2.87
16 Aug.	1.14	3.02	4.17
1 Sept.	1.26	2.55	3.82
22 Sept.	1.40	1.82	3.22
13 Oct.	1.44	1.02	2.46
27 Oct.	1.23	2.16	3.39
		1980	
10 May	1.10	2.17	3.26
7 June	0.83	1.74	2.56

Within the SML and DL, dissolved and particulate concentrations of Pb-210 were integrated to determine total dpm distributions in each layer. The volume of water was estimated for each layer and the concentrations (dpm/liter) computed. Standing crops of Pb-210 (dpm/cm^2) were calculated by multiplying concentration by layer height. That is,

$$\text{Standing crop (dpm/cm)} = \frac{\Sigma \text{DPM}}{V} \cdot Z \qquad (12)$$

where:

Z is the mean layer height (cm), V is the volume of water (cm^3), ΣDPM represents the estimated total dissolved or particulate Pb-210 in the layer

$$\Sigma \text{EPM} = \int_{z_1}^{z_2} \text{Pb.}\, dz$$

evaluated at 1-m intervals as an approximation.

The standing crops of Pb-210 in each layer were calculated using Eq. (12) and are presented in Table 14. Although reservoir sizes varied slightly between a few sampling dates during the stratified period, the effects on the estimated standing crop is small (c.a., 5 to 10%).

TABLE 14. DISSOLVED AND PARTICULATE PHASE STANDING CROPS OF Pb-210 (dpm/cm^2) IN CRYSTAL LAKE. THE TOTAL STANDING CROP IS EXPRESSED AS THE SUM OF DISSOLVED AND PARTICULATE PHASES

Date	Depth interval (m)	Dissolved	Particulate	Total
	Surface Mixed Layer			
5 June 1979	0-10	0.035	0.141	0.176
23 June 1979	0-6	0.022	0.132	0.154
11 July 1979	0-6	0.012	0.042	0.054
16 Aug. 1979	0-8	0.037	0.094	0.131
1 Sept. 1979	0-8	0.040	0.067	0.107
22 Sept. 1979	0-10	0.044	0.049	0.093
13 Oct. 1979	0-10	0.048	0.032	0.080
27 Oct. 1979	0-10	0.043	0.071	0.114
10 May 1980	0-10	0.040	0.074	0.114
7 June 1980	0-10	0.030	0.059	0.089
	Deep Layer			
5 June 1979	10-21	0.041	0.078	0.119
23 June 1979	6-21	0.032	0.170	0.202
11 July 1979	6-21	0.029	0.114	0.143
16 Aug. 1979	8-21	0.033	0.092	0.125
1 Sept. 1979	8-21	0.036	0.105	0.141
22 Sept. 1979	10-21	0.054	0.087	0.141
13 Oct. 1979	10-21	0.047	0.039	0.086
27 Oct. 1979	10-21	0.036	0.074	0.110
10 May 1980	10-21	0.030	0.069	0.099
7 June 1980	10-21	0.021	0.054	0.075

As a first approximation fluid exchange across the SML-DL boundary is neglected (Imboden and Lerman 1978). A further assumption is made that the dissolved diffusive exchange of Pb-210 between the SML and DL is small compared to transport of particulate Pb-210 between the layers. Craig et al. (1973) have shown that this is the case in the Pacific Ocean. Erickson (1980), working on P dynamics in Fish Lake (Wisconsin)--a lake with approximately the same surface area and depth as Crystal Lake--found that diffusion-mediated vertical transport of dissolved P was unimportant compared to particulate P transport.

A simple calculation demonstrates that dissolved Pb-210 fluxes across the SML-DL boundary can be neglected in Crystal Lake. An average eddy diffusivity of heat in the thermocline region of most lakes is about 0.01 cm^2/sec (Imboden and Lerman 1978). Colman (1979) estimated K_z based on Rn-222 gradient profiles near the bottom of Crystal Lake under ice-covered conditions and found K_z to be about 0.001 cm^2/sec. The mean dissolved Pb-210 gradient observed between the SML and DL was 0.2 dpm/100 liters/m during the stratified period based on estimated vertical concentration differences. The vertical flux of dissolved Pb-210 can be calculated at the metalimnion-epilimnion (SML-DL) boundary by evaluating:

$$U = K_z \frac{dc}{dz} \qquad (13)$$

where:

U is the dissolved diffusive flux

dc/dz is the dissolved Pb-210 gradient

K_z is the vertical eddy diffusivity.

The vertical flux of dissolved Pb-210 computed using Eq. (13) is 0.006 dpm/cm^2/yr. It will be shown later that the flux of Pb-210 by particulate phase transport is 10^2 to 10^3 times greater than the dissolved flux estimated here. The value of 0.01 cm^2/sec used for K_z in the previous calculation is an eddy diffusion coefficient commonly found for heat in thermoclines of small lakes (Sweers 1970, Jassby and Powell 1975, Imboden and Emerson 1978, Quay et al. 1980). Quay et al. (1980) studied the relationship between K_z for heat and mass (dissolved ions) in several small stratified lakes located in the Experimental Lakes Area (ELA) of northwestern Ontario, Canada. It was suggested that the K_z for mass is probably closer to molecular diffusion rates which are of the order of 10^{-5} cm^2/sec in the thermocline region. If K_z was reduced by one or two orders of magnitude in the present calculation, the dissolved flux would become vanishingly small. Thus, even in the face of deliberate overestimation of K_z (and probably dc/dz), diffusion-mediated transport of dissolved Pb-210 can be neglected.

During unstratified conditions the exchange of dissolved Pb-210 between the surface and deeper water is expected to occur rapidly (large K_z) so that all vertical inhomogeneities would disappear. It is commonly assumed that for the unstratified period the system can be described by a one-box model (Imboden and Lerman 1978). As alluded to earlier, this does not seem to be the case for Crystal Lake during the interval studied here. A dissolved gradient always existed between surface and deep water. The standing crop estimates presented in Table 14 suggest that the lake is well mixed only immediately after fall turnover (27 October 1979). Temperature profiles (Figure 7) also indicate that the lake was well mixed only at this time. Since the lake is well protected from wind by a pine tree forest, there may be insufficient wind-induced turbulence to drive complete mixing of the water column. In addition, standing crops of particulate phase Pb-210 are much greater than corresponding dissolved standing crops. The assumption is made that the dissolved flux is small compared to particulate phase transport even under unstratified conditions. Consequently, the lake can be modeled as a two-layer system throughout the interval studied.

DESCRIPTION OF THE TWO-LAYER MODEL

For each of the layers, the change in standing crop of Pb-210 as a function of time is given by:

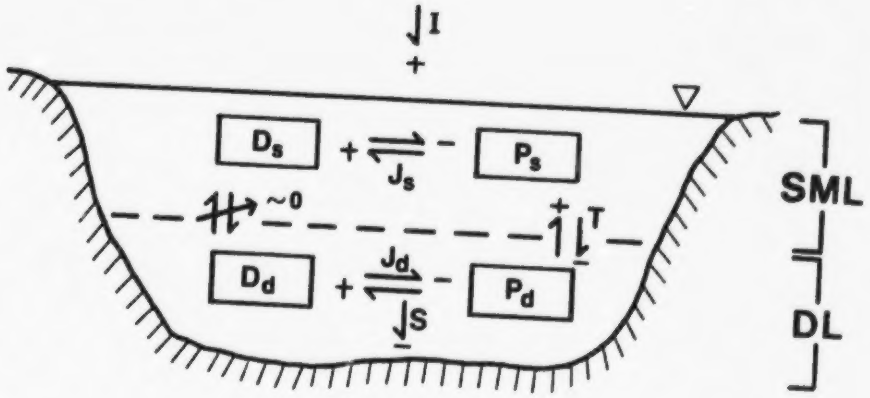
$$\frac{d}{dt}\Sigma Pb = \frac{d}{dt}\int_{z_1}^{z_2} Pb \cdot dz. \qquad (14)$$

As a method of estimating ($\frac{d}{dt}\Sigma Pb$) material mass balances are constructed for dissolved and particulate phases. The material mass balance relationships are summarized in Figure 26. Units of dpm/cm^2 were chosen so that dissolved and particulate phases in the SML and DL can be compared directly. Net transfer between dissolved and particulate phase is represented by J, which is taken to be positive when transfer is from particulate to dissolved phase. Removal (-) or gain (+) of Pb-210 is considered to occur exclusively by particulate transport which is represented by T in the SML and S in the DL.

In the SML for dissolved Pb-210:

$$D_{t_2} = D_{t_1} + J_s + I \qquad (15)$$

which states that the dissolved standing crop at time t_2 must be equal to the standing crop at an earlier time t_1, plus atmospheric input I to the SML between t_1 and t_2, and transfer of Pb-210 to solution from the particulate phase. Radioactive decay of Pb-210 over the time interval considered in the model can be neglected. Production of Pb-210 *in situ* from decay of Ra-226 is of the order of 0.001 dpm/cm^2 and can be neglected. Incidentally, the


I
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-
D_d
+
J_d
-
P_d
S
-
SML
DL

Surface Mixed Layer

$$D_{T_2} = D_{T_1} + J_S + I$$

$$P_{T_2} = P_{T_1} - J_S + T$$

Deep Layer

$$D_{T_2} = D_{T_1} + J_d$$

$$P_{T_2} = P_{T_1} - J_d - T + S$$

Figure 26. Representation of the two-layer model used to examine transport dynamics of Pb-210 in Crystal Lake.

decay of Pb-210 over a 1 yr interval is about 2% which essentially cancels out the *in situ* production of PB-210 in the standing crop estimate (~ 2%).

The atmospheric input I is considered here in the dissolved phase material mass balance (Eq. 15). If we assume that atmospheric Pb is primarily in the form of carbonates, oxides, and halides (Ter Haar and Bayard 1971), a large fraction of the Pb in rain water would be dissolved at a pH < 5 (Stumm and Morgan 1970). In addition, dry deposition of Pb-210 is small compared to wet deposition (Section 8) and the SML is slightly acidic (pH ≈ 6.0) favoring release of newly deposited aerosol Pb-210 into solution. These data, plus the fact that a large fraction of aerosol Pb-210 is readily soluble in neutral pH solutions (Hodge et al. 1978) suggest that the correspondence between atmosphere and SML is mediated primarily by dissolved phase interactions.

Thus, it has been assumed in the model calculations that the atmospheric input of Pb-210 to Crystal Lake occurs by dissolved phase transfer. In calculating the amount of removal or gain of particulate Pb-210 in the SML it makes no difference whether the input is considered dissolved or particulate (i.e., the value of T does not change in Eq. 16). The net transfer term J_s is affected, however, by the choice of the input mechanism. As a result of the dependence of J_s on the input mechanism, the estimate of the residence time of dissolved material in the SML has a maximum uncertainty of 20 to 50%.

Numerical substitution of values into Eq. (15) and the other mass balance relationships (Eqs. 16 to 18) is made directly from Table 14. The average per-interval atmospheric input I is taken to be equal to 0.10 dpm/cm^2 (See Section 8 and Table 16). As an example consider the interval 23 June 1979 (t_1) to 11 July 1979 (t_2). Substitution of values into Eq. 15 gives:

$$0.012 = 0.022 + J_s + 0.10$$

$$J_s = -0.11 \text{ dpm/cm}^2.$$

The net flux J_s is negative, indicating Pb-210 was transferred from solution to particulate phase during this period.

For particulate Pb-210, a similar mass balance can be written incorporating particulate phase transport T. Thus,

$$P_{t_2} = P_{t_1} - J_s + T \qquad (16)$$

which says that particulate phase Pb-210 at time t_2 is determined by its standing crop at t_1, transfer from solution, and most importantly transport of particulate Pb-210 between the SML and DL. For particulate phase Pb-210:

$$0.042 = 0.13 + 0.11 + T$$

$$T = -0.20 \text{ dpm/cm}^2.$$

Since T is negative, particulate Pb-210 was transferred from the SML to the DL. It is assumed that a negligible amount of Pb-210 deposits in the littoral zone. This is probably a reasonable assumption for Crystal Lake due to the fact that the majority of the SML lies in the pelagic zone of the lake. In addition, the area of the littoral zone of Crystal Lake is small compared to the area of the pellagic zone.

Consider the dissolved Pb-210 mass balance in the DL:

$$D_{t_2} = D_{t_1} + J_d. \qquad (17)$$

Substitution of numerical values leads to:

$$0.029 = 0.032 + J_d$$

$$J_d = -0.003 \text{ dpm/cm}^2.$$

As was the case in the SML, Pb-210 was transferred to the particulate phase. Finally, the mass balance for particulate Pb-210 in the DL is

$$P_{t_2} = P_{t_1} - J_d - T + S \qquad (18)$$

and

$$0.11 = 0.17 + 0.003 + 0.20 + S$$

$$S = -0.26 \text{ dpm/cm}^2.$$

Here, S is negative and its magnitude compared to I suggests that a rather large loss of Pb-210 occurred from the water column. In addition, reasonable agreeement between T and S exists which should be the case under truly steady-state conditions.

RESULTS OF THE TWO-LAYER MODEL

Correspondence Between Input and Removal

The results of the two-layer model calculations for the 1-yr interval 5 June 1979 to 7 June 1980 are presented in Table 15. The values of T and S were calculated for Pb-210 assuming a constant average atmospheric input of 0.10 dpm/cm^2. To express J, T, and S in terms of mean fluxes, enter the time factor since $\Delta t = t_2 - t_1$. Thus T and S are in units of dpm/cm^2/yr.

TABLE 15. RESULTS OF THE TWO-LAYER MODEL FOR Pb-210 USING AN AVERAGE PER-INTERVAL ATMOSPHERIC INPUT OF 0.10 dpm/cm^2.

Interval	(-) T		(-) S	
(1979-80)	dpm/cm^2	dpm/cm^2/yr	dpm/cm^2	dpm/cm^2/yr
5 June to 23 June	0.12	2.41	0.037	0.75
23 June to 11 July	0.20	4.06	0.26	5.25
11 July to 16 Aug.	0.023	0.23	0.041	0.42
16 Aug. to 1 Sept.	0.12	2.83	0.10	2.37
1 Sept. to 22 Sept.	0.11	1.98	0.11	1.91
22 Sept. to 13 Oct.	0.11	1.97	0.17	2.87
13 Oct. to 27 Oct.	0.071	1.85	0.047	1.22
27 Oct. to 10 May 0.097	0.18	0.11	0.20	
10 May to 7 June 0.13	1.62	0.15	2.00	
Mean	0.11 ± 0.05	1.90 ± 1.21	0.11 ± 0.07	1.89 ± 1.55

It is evident from the model estimates of T and S that large temporal variations exist in the removal rate of Pb-210 from the water column. These data suggest that non-steady-state processes strongly influence removal of Pb-210 from the lake.

By averaging the values of T and S over the 1-yr interval an estimate of net sedimentation during this period was made. For the 1979 to 1980 interval considered the mean sedimentation of Pb-210 was 0.11 dpm/cm^2 or in terms of flux 1.90 dpm/cm^2/yr. It is apparent from the model estimates of T and S presented in Table 15 that T and S are equal when considered over the 1-yr period, indicating that steady-state assumptions are valid on a time scale of approximately 1 yr for Crystal Lake.

To examine the correspondence between atmospheric input of Pb-210 and its removal from the water column over short time intervals (i.e., less than 1 month), the value of I in the model equations was varied. Wet deposition of Pb-210 was measured directly with a time resolution of about 2 weeks during the period 5 June to 22 September 1979. The integrated rainfall samples were spaced over the same collection intervals as the Pb-210 water column profiles. Dry deposition estimates are not available for such short time intervals due to the limitations of sampling. For this reason, a constant average dry deposition of 0.01 dpm/cm^2 was used in all model calculations (Section 8). Wet deposition estimates were taken directly from Table 8.

A comparison of the atmospheric input and in-lake seidmentation of Pb-210 over short time interals is shown in Table 16. The interval 5 June to 22 September 1979 roughly corresponds to the stratified period. For the unstratified period 22 September 1979 to 7 June 1980, a constant atmospheric

TABLE 16. RESULTS OF THE TWO-LAYER MODEL FOR Pb-210 USING AN AVERAGE DRY DEPOSITION OF 0.02 dpm/cm^2 AND A VARIABLE WET DEPOSITION FOR THE INTERVALS 5 JUNE TO 23 JUNE THROUGH 1 SEPTEMBER TO 22 SEPTEMBER. AN AVERAGE PER-INTERVAL ATMOSPHERIC INPUT OF 0.10 dpm/cm^2 WAS USED FOR THE INTERVALS 22 SEPTEMBER TO 13 OCTOBER THROUGH 10 MAY TO 7 JUNE

Interval	I	(-) T		(-) S	
(1979-80)	dpm/cm^2	dpm/cm^2	dpm/cm^2/yr	dpm/cm^2	dpm/cm^2/yr
5 June to 23 June	0.15	0.17	3.43	0.087	1.77
23 June to 11 July	0.07	0.17	3.45	0.23	4.65
11 July to 16 Aug.	0.13	0.058	0.59	0.076	0.77
16 Aug. to 1 Sept.	0.05	0.074	1.69	0.058	1.32
1 Sept. to 22 Sept.	0.05	0.064	1.11	0.064	1.11
22 Sept. to 13 Oct.	0.10	0.11	1.97	0.17	2.87
13 Oct. to 27 Oct.	0.10	0.071	1.85	0.047	1.22
27 Oct. to 10 May	0.10	0.097	0.18	0.11	0.20
10 May to 7 June	0.10	0.13	1.62	0.15	2.00
Mean ± S.D.	0.10 ± 0.03	0.11 ± 0.04	1.77 ± 1.12	0.11 ± 0.06	1.77 ± 1.32

input of 0.10 dpm/cm^2 was used due to the lack of sufficient time resolution in estimates of atmospheric input.

The results of the model calculations shown in Table 16 probably portray the in-lake dynamics of Pb-210 more accurately than estimates of T and S obtained by holding the atmospheric parameter I constant (Table 15). The annual mean estimates of T and S are, of course, approximately the same in both cases.

Although it appears that steady-state conditions may exist on a long-term basis, it is evident that non-steady-state processes affect input and removal of Pb-210 on a short-term basis. The value of S, for example, varies by a factor of almost 25 (Table 16). A comparison of the parameters I, T, and S for a particular system generally is not available. This study provides a look at the correspondence between these parameters on a short-term basis.

A comparison of I, T, and S for Crystal Lake is presented in Table 17. Note that the values of I, T, and S vary by a factor of 3 to 4 over the stratified period. To conveniently compare input and removal of Pb-210 during the stratified period, the ratios T:I and S:I are shown for specific time periods. A value of 329% for the ratio S:I during the interval 23 June to 11 July 1979 suggests that this was a period of high sedimentation of Pb-210. This event, in fact, removed almost twice as much Pb-210 from the water column as all other periods combined (Table 13). For the last 2 months of the stratified period (16 August to 22 September 1979) the removal of Pb-210 was much slower with S just balancing I (average S:I ≈ 100%).

TABLE 17. COMPARISON OF ATMOSPHERIC INPUT AND PARTICULATE PHASE REMOVAL FROM THE WATER COLUMN DURING THE STRATIFIED PERIOD. VALUES OF T, S, AND I ARE TAKEN FROM TABLE 16

Interval (1979)	(-) T (dpm/cm^2)	(-) S (dpm/cm^2)	I (dpm/cm^2)	T:I (%)	S:I (%)
5 June to 23 June	0.17	0.087	0.15	113	58
23 June to 11 July	0.17	0.23	0.07	243	329
11 July to 16 Aug.	0.058	0.076	0.13	45	58
16 Aug. to 1 Sept.	0.074	0.058	0.05	148	116
1 Sept. to 22 Sept.	0.064	0.064	0.05	128	128

The removal of Pb-210 was faster during the stratified period than the unstratified period. The estimates of I, T, S, and S' presented in Table 18 bear this out. The parameter S' represents the flux of particulate Pb-210 determined from the sediment trap study. Values of T and S were taken from Table 16.

TABLE 18. COMPARISON OF ESTIMATES FOR THE PARAMTERS I, T, S, AND S'. CONFIDENCE LIMITS FOR THE MEAN WERE CALCULATED AT THE 95% LEVEL

Parameter	Mean	
	dpm/cm^2	dpm/cm^2/yr
I, rain	0.08 ± 0.04	1.58 ± 0.76
I, dry	0.02	0.21
I, total	0.10	0.79
T, stratified	0.11 ± 0.05	2.05 ± 1.16
T, unstratified	0.10 ± 0.02	1.41 ± 0.81
S, stratified	0.10 ± 0.03	1.92 ± 1.37
S, unstratified	0.12 ± 0.05	1.57 ± 0.57
S', stratified	0.15 ± 0.02	2.28 ± 0.44
S', unstratified	0.11 ± 0.03	1.15 ± 0.35

A close agreement exists between the average input and removal rate of Pb-210 from Crystal Lake indicating that the amount of Pb-210 produced *in situ* from decay of Ra-226 is small compared to the atmospheric supply of unsupported Pb-210. This can be used as a first approximation to verify the assumption of negligible *in situ* production of Pb-210 in the material mass balances (Eqs. 15 to 18).

Based on S', the flux of Pb-210 was almost twice as much during the stratified period as the unstratified interval. These differences in S' are significant at the $\alpha = 0.05$ level. The difference in S between these two periods is small, but the difference is significant at the $\alpha = 0.05$ level. These differences in S and S' between the two periods suggests that in-lake processes have various efficiencies in removing Pb-210 from the water column. Biological processes operating during the productive stratified period are apparently more effective in removing Pb-210 from the water column than processes during the languid unstratified interval. A positive correlation between biological productivity and the removal rate of Pb-210 also has been observed in the ocean (Thomson and Turekian 1976). Some of the biological, chemical, and physical factors which are believed to cause non-steady-state conditions in Crystal Lake will not be examined in greater detail.

Correlation of Particulate Removal With In-Lake Processes

Particulate phase Pb-210 reached the highest levels in the SML during the June and August plankton blooms. It was not until late in the blooms (or after) that particulate Pb-210 increased in the DL. In addition, a lag existed in the decrease of particulate Pb-210 in the DL compared to the SML (Table 14). This suggests that bloom-related biogenic debris with net settling velocities < a few tenths meter/day (Riley 1970) was lingering in the DL. Apparently much of this Pb-210 is recycled in the DL, as the sedimentation of Pb-210 over the months following the bloom was small compared to the annual mean deposition of Pb-210. This recycling process is most evident after the August bloom, where much of the bloom-related particulate Pb-210 appeared to be released to the dissolved phase in the DL (1 to 22 September 1979). Consequently, little Pb-210 reached the sediment (Table 16).

During the June bloom the rate of removal of Pb-210 from the SML averaged 3.44 dpm/cm^2/yr. The deposition of Pb-210 from the DL, however, did not increase above the annual mean flux of 1.77 dpm/cm^2/yr (Table 16). Most of the deposition occurred over the short interval following the bloom (23 June to 11 July 1979). During this interval the sedimentation of Pb-210 was estimated to be 4.65 dpm/cm^2/yr. This rate of removal is about 2.5 times greater than the annual mean deposition of Pb-210 in Crystal Lake.

The decrease in standing crop of particulate Pb-210 is strongly correlated with the drop in SPM standing crop (Table 19). These effects are attributed to bloom die-off. The experimental data suggest that plankton themselves (*Staurastrum*) are conveying Pb-210 to the sediment directly. If zooplankton fecal pellet deposition removed substantial amounts of Pb-210 during the bloom period, it is expected that a large sedimentation of Pb-210 would have been seen from 5 to 23 June 1979. Fecal pellets have settling velocities of up to several hundred m/day (Komar et al. 1981) and would easily reach the botoom of Crystal Lake in a day or so. Some deposition of Pb-210 by fecal pellet exudation undoubtedly took place. However, these "instantaneous fluxes" do not appear to be as important for cleansing the water column of Pb-210 as the event-type depositional processes.

TABLE 19. SUSPENDED PARTICULATE MATTER STANDING CROPS

Profile date	SML (μg/cm^2)	DL (μg/cm^2)	Mean (μg/cm^2)
5 June 1979	980	1122	1051
23 June 1979	922	1112	1017
11 July 1979	326	652	489
16 August 1979	987	1029	1008
1 September 1979	541	795	668
22 September 1979	316	837	577
13 October 1979	261	758	510
27 October 1979	461	493	477
10 May 1980	490	865	678
7 June 1980	193	470	331

Experimental evidence supports the supposition made here that phytoplankters may have carried enormous amounts of Pb-210 as they settled to the bottom of Crystal Lake. Most phytoplankton are slightly more dense than water (1.01 to 1.1 g/cm^3) and sink at a measurable rate (Titman 1975, Bienfang 1979). The sinking rate is a function of the physiological state of the cell and is apparently not a species specific constant (Eppley et al. 1967, Smayda 1974). Eppley et al. (1967) found that the fastest sinking rate (> 1 m/day) was correlated with declining physiological activity. Titman and Kilham (1976) suggested that the cells sink at rates dependent on nutrient uptake. They found that nutrient depleted cells settle much more rapidly than exponentially growing cells. Sinking rates as fast as 6.8 m/day were observed for phytoplankters in the stationary growth phase. Higher settling rates also are characteristic of larger planktonic species (Smayda 1970).

In Crystal Lake the removal of Pb-210 was correlated with bloom die-off suggesting that *Staurastrum*-dominated phytoplankters removed particulate phase Pb-210 from the lake as they died and settled to the bottom. Since *Staurastrum* are relatively large phyotplankters (Nalewajo 1966), they probably have sinking rates of the order of several m/day in their stationary growth phase. The sinking rate probably increases as they die. These phytoplankters seem to possess the efficacious ability to convey Pb-210 from the SML to the sediments in the 18-day period 23 June to 11 July 1979.

The deposition of Pb-210 by settling pine pollen also must be considered as a removal mechanism for the June to July period. Pine pollen floats on the lake surface until its air bladder is ruptured and fills with water. In the lake this may happen by mechanical breakage or after attack by bacteria (Davis and Brubaker 1973). Once this occurs, the density of the grain increases from 0.8 to 1.2 g/cm^3 and the pollen sinks rapidly (Brush and Brush 1972).

Most of the pine pollen observed in the water column of Crystal Lake appeared to still have air in the bladders. These pollen were apparently transported to depth by turbulent water mixing processes before the lake became thermally stratified (i.e., prior to 23 June 1979). The air is eventually expelled from these pollen and they sink to the bottom. Pine pollen comprises a major portion of the sediment in Crystal Lake (Conger 1939, Twenhofel and Broughton 1939). Pollen grains thus represent a vehicle for transporting material to the sediment. Brush and Brush (1972) determined the settling velocity of water saturated pine pollen to be about 26 m/day. This means that once the grains have become wetted they sink rapidly to the bottom of Crystal Lake within 1 or 2 days. In this sense, pollen grains act much like zooplankton fecal pellets.

Microscopic examination of SPM collected on 11 July 1979 revealed that pine pollen was still abundant in the water column. Some of this pollen was probably fresh input to the lake, particularly in the SML. Most of the grains observed in the DL were most likely in transit to the sediment.

Since the water sampling missed the sedimentation event, no direct evidence exists for a deposition mechanism. It seems reasonable to postulate that plankton carried most of the Pb-210 to the bottom directly. Deposition of Pb-210 by fecal pellets and pine pollen most likely also contributed to the June to July sedimentation event. It appears that these mechanisms were of minor importance in depositing Pb-210. The pollen, however, may be related to deposition in another sense. The input of pollen to the nutrient poor lake waters may have provided the nutrient stimulation (e.g., P) necessary to commence the plankton bloom.

If the assumption is made that most of the increase of particulate Pb-210 observed during June was associated with plankton, the standing crop of plankton Pb-210 can be estimated as follows (Table 14):

	Particulate Pb-210	
	SML	DL
Bloom	0.137	0.170
Non-bloom	-0.053	-0.102
Plankton Pb-210 (dpm/cm^2)	0.084	0.068

The mean differences between bloom and non-bloom standing crops of particulate Pb-210 (stratified period) indicate that the average plankton Pb-210 was in the neighborhood of 0.076 dpm/cm^2. The mean particulate Pb-210 during the bloom was 0.148 dpm/cm^2. Thus, about 50% of the particulate Pb-210 was associated with plankton (43% of total Pb-210).

Examining the period 23 June to 11 July 1979, the decrease of particulate Pb-210 attributed to the bloom die-off can be estimated. In the SML, a decrease of 0.132 - 0.042 = 0.090 dpm/cm^2 occurs, and in the DL 0.170 - 0.114 = 0.056 dpm/cm^2 (Table 14). The average decrease was 0.073 dpm/cm^2, which is essentially the same as the estimated standing crop of plankton Pb-210. Furthermore, the standing crop of total Pb-210 declined 51% (Table 13) in the same June to July period. This prodigious loss of Pb-210 is ascribed primarily to the activities of the biosphere. Although these calculations are speculative, they at least demonstrate that Pb-210 was removed effectively from the water column. Unlike the August bloom, there appears to have been such complete removal of Pb-210 that only small amounts of particulate Pb-210 remained in the DL. Thus, little Pb-210 associated with the bloom appears to have been recycled in the lake.

Direct measurement of plankton Pb-210 was performed on plankton collected during the mid-August bloom. The standing crop of SPM again reached the 1000 μg/cm^2 level. This suggests that the biomass was essentially the same as in the June period. The weighted mean activity of Pb-210 in plankton (phytoplankton and zooplankton) was 12.0 dpm/g. The plankton biomass was estimated to be 535 μg/cm^2 (Section 7). The standing crop of plankton Pb-210 can be estimated as:

$$12 \text{ dpm/g} \times 534 \ \mu\text{g/cm}^2 \times 10^{-6} \text{ g}/\mu\text{g} = 0.006 \text{ dpm/cm}^2.$$

From Table 14 it can be seen that the mean standing crop of particulate Pb-210 in the lake was 0.093 dpm/cm^2 on 16 August 1979 suggesting that plankton Pb-210 comprised 6% of the particulate Pb-210 (5% of total Pb-210). Holm (1978) found that Cd, Cu, and Zn in plankton collected from six southern California lakes accounted for about 1% of the total metal in these lakes.

Assuming that the June and August biomasses were similar in magnitude, the August standing crop of plankton Pb-210 was much lower than during the June bloom. The planktonic species associated with the August bloom apparently did not concentrate Pb-210 to the degree that June plankton did. Using a standing crop of 0.076 dpm/cm^2 for the June plankton Pb-210 and a biomass of 500 μg/cm^2, the plankton Pb-210 concentration must have been around 150 dpm/g. This is at least 10 times higher than observed for the August bloom (12 dpm/g). These calculations suggest that the August plankton may have acted in the capacity of recyclers of Pb-210 rather than carriers. Holm (1978) used integrated rate equations to model uptake and release of Cd, Cu, and Zn from plankton. The data suggest that rates of release of metals from plankton were roughly equal to the rate of uptake.

The removal of Pb-210 was not nearly as extensive in August as it was in the June to July period despite the similar decreases in standing crop of SPM. The ratio S:I clearly bears this out (Table 17), being several hundred percent lower after the August bloom compared to the June to July period. The total standing crop of Pb-210 decreased by 8% after the August bloom (16 August to 1 September 1979). This suggests that the plankton Pb-210 was rapidly removed from the lake. A closer look at the data suggests otherwise.

Following the bloom there was a loss of particulate Pb-210 from the SML. The DL experienced a net gain of particulate Pb-210, which was later released to the dissolved phase and recycled when fall turnover occurred. Thus, it is difficult to tell from the experimental data what fraction of the plankton Pb-210 was recycled and how much was deposited directly to the sediment.

The rate of sedimentation of Pb-210 associated with the August bloom was 30% less than the annual mean deposition rate. This is in glaring contrast to the deposition of Pb-210 after the June bloom where the sedimentation rate was 2.6 times greater than the annual mean deposition of Pb-210. These results indicate that the specific characteristics of the water column are of the utmost importance in controlling the dynamics of in-lake Pb-210 cycling.

The second largest removal of Pb-210 from the water column of Crystal Lake occurred during fall turnover (22 September to 13 October 1979). The rate of removal was more than 1.5 times the annual mean deposition rate of Pb-210. The standing crop of SPM decreased slightly (Table 19) indicating that little resuspension of bottom sediments was associated with fall turnover. However, a large decrease in particulate Pb-210 was observed while the dissolved phase remained essentially unchanged, suggesting that deposition of particulate Pb-210 was rapid. Also the major part of the particulate Pb-210 was removed from the DL (Table 14). The explanation offered is that small debris (detritus, etc.), which was trapped in the SML during stratification, was released upon mixing (Hutchinson 1957) and subsequently aggregated particles in the DL. These large aggregated masses rapidly transcended the DL, efficiently removing particulate phase Pb-210. Apparently the removal was so rapid that little scavenging of dissolved Pb-210 occurred, or the sampling complete missed the phenomena.

The lake quickly recovered from this loss of Pb-210, and standing crops of dissolved and particulate phase Pb-210 became equal in the SML and DL by 27 October 1979. The period after fall turnover appears to be biologically unproductive and can be characterized as the lake's closest approach to steady-state conditions with respect to supply and removal of Pb-210. This suggests that changes from the standing crops of Pb-210 are the result of biological, chemical, and physical factors. The effects of these factors can be illustrated by estimating the mean residence times of Pb-210 in dissolved and particulate phases. These residence times ($\bar{\tau}$) have been calculated with respect to removal (i.e., negative values of J, T, and S) and are shown in Table 20. Blank spaces appearing in Table 20 represent periods where the values of J, T, or S were positive indicating a net gain of Pb-210.

Uncertainty is associated with the model estimates of $\bar{\tau}_{d,s}$ due to the fact that the atmospheric input was assumed to contribute exclusively to dissolved phase Pb-210 in the SML. If all the input had been assumed to be the particulate phase, the value of $\bar{\tau}_{d,s}$ would increase by about 20% for the stratified period. An increase of almost 50% would be in order for the unstratified period. These increases represent the maximum change in estimated value of $\bar{\tau}_{d,s}$. The true change in the value of $\bar{\tau}_{d,s}$ would, in fact, not be as great at 20 to 50% since some atmospheric input actually occurs to both dissolved and particulate phases. The stated uncertainties in the value of $\bar{\tau}_{d,s}$ are unimportant in terms of the interpretation of the experimental data. Since wet deposition of Pb-210 greatly exceeds the dry input and it is likely that a large fraction of Pb-210 in rain (pH $<$ 5) is dissolved, it was felt that an acceptable estimate of $\bar{\tau}_{d,s}$ was obtained.

In general, residence times of 1 month or less are associated with periods of elevated biological activity in Crystal Lake. The longest residence times, of the order of a few tenths year or greater, are characteristic of the more unproductive periods where perturbations of the Pb-210 geochemical cycle are less pronounced. These differences in residence times are summarized in Table 21.

The overall annual mean residence time of Pb-210 in Crystal Lake is 0.20 yr, the same as that estimated for Pb (Section 7). During the stratified period the residence time of Pb-210 is usually $\leq$ 0.10 yr. The opposite it true for the unstratified interval, where the residence time is greater than few tenths year. The difference in residence times between the two periods demonstrates the varying efficiency and intensity of depositional mechanisms.

TABLE 20. RESIDENCE TIMES OF DISSOLVED AND PARTICULATE PHASE Pb-210 IN CRYSTAL LAKE ESTIMATED FROM THE TWO-LAYER MODEL. RESIDENCE TIMES ARE CALCULATED WITH RESPECT TO MEAN REMOVAL OF Pb-210

Interval	$\bar{\tau}_{d,s}$[a] (yr)	$\bar{\tau}_{p,s}$ (yr)	$\bar{\tau}_{d,d}$ (yr)	$\bar{\tau}_{p,d}$ (yr)
5 June to 23 June	0.009	0.040	0.203	0.070
23 June to 11 July	0.010	0.025	0.500	0.031
11 July to 16 Aug.	0.023	0.115	-	0.134
16 Aug. to 1 Sept.	0.036	0.048	-	0.075
1 Sept. to 22 Sept.	0.053	0.052	-	0.086
22 Sept. to 13 Oct.	0.028	0.021	0.421	0.022
13 Oct. to 27 Oct.	0.017	0.028	0.143	0.046
27 Oct. to 10 May	0.218	0.403	3.00	0.358
10 May to 7 June	0.024	0.041	0.213	0.031

[a] First subscript denotes dissolved (d) or particulate (p) phase; second subscript denotes SML (s) or DL (d).

Explanation of terms:

Let $\bar{D} = \frac{1}{2} (D_{t_1} + D_{t_2})$ and $\bar{P} = \frac{1}{2} (P_{t_1} + P_{t_2})$

Then when J, T, or S are negative:

$$\bar{\tau}_{d,s} = \bar{D}/-J_s \quad \text{and} \quad \bar{\tau}_{p,s} = \bar{P}/-T$$

$$\bar{\tau}_{d,d} \equiv \bar{D}/-J_d \quad \text{and} \quad \bar{\tau}_{p,d} = \bar{P}/-S$$

TABLE 21. MEAN RESIDENCE TIMES (YR) OF DISSOLVED AND PARTICULATE PHASE Pb-210 IN CRYSTAL LAKE FOR THE STRATIFIED AND UNSTRATIFIED PERIODS

Interval	Dissolved Pb-210		Particulate Pb-210	
	SML	DL	SML	DL
Stratified	0.025	0.30	0.046	0.054
Unstratified	0.22	3.0	0.40	0.36

The residence time of particulate Pb-210 is around 0.05 yr in the SML and DL suggesting that the major portion of the particulate Pb-210 in the lake is associated with specific particle types. The interaction of dissolved and particulate phase Pb-210 appears to be the most intimate in the SML. The residence time of dissolved Pb-210 in the SML was highly variable and generally less than the residence time of particulate Pb-210. The behavior of dissolved Pb-210 in the DL is more conservative than in the SML. Dissolved Pb-210 in the DL appears to be affected little by plankton blooms, which suggests that most of the Pb-210 is scavenged by primary producers in the SML. The residence time of dissolved Pb-210 in the SML is consequently about an order of magnitude less than in the DL. The difference in residence times of dissolved Pb-210 in the two layers during the unstratified period is evidence that the lake was not well mixed. This suggests that a lack of communication exists between these layers. It seems appropriate, therefore, to consider the lake as a two-layer system throughout the year.

A brief comment about the interval 27 October 1979 to 10 May 1980 seems justified. During this wintertime interval no sampling was conducted to characterize the dissolved or particulate phase Pb-210 distributions. The standing crop of dissolved and particulate Pb-210 was essentially unchanged on 10 May 1980 from the preceding fall period. Consequently, the estimated deposition of Pb-210 from 27 October 1979 to 10 May 1980 was small (Table 16). Immediately after ice-out (late April) there was probably a large input of Pb-210 assocaited with winter accumulation of Pb-210 during ice cover. Apparently the in-lake deposition of Pb-210 was rapid as no signs of the event were present on 10 May 1980. Although the event was not captured by the sampling, it was probably significant in terms of the amount of Pb-210 deposited.

POSSIBLE SOURCES OF Pb-210 TO CRYSTAL LAKE

Crystal Lake is a seepage lake and discharge of ground water could contribute Pb-210 to the water column. However, this potential source of Pb-210 usually is negligible compared to Pb-210 activities in receiving water (Lewis 1977, Benninger 1978). The low activity ratios of Pb-210:Ra-226 in ground water suggest the residence time of Pb-210 is short relative to the long hydraulic residence time of ground water (Holtzman 1964). Lead-210 appears to be quickly adsorbed on rocks close to its point of injection into ground water (Benninger et al. 1975) suggesting ground water probably contributes little Pb-210 directly to the water column of Crystal Lake. In addition, Pb-210 is efficiently scavenged by particles as the ground water seeps slowly through the sides of the lake.

Insufficient data presently is available to estimate ground water flow around Crystal Lake. A rough estimate with regard to the water balance can be made. The area immediately around Crystal Lake receives about 80 cm of rainfall annually (unpublished data, 1972 to 1979, collected at Boulder Junction, Wisconsin, Wisconsin Department of Natural Resources Forestry Headquarters). Hutchinson (1957) reports that the average evaporation from Lakes Huron and Michigan during the May to October period is 0.164 cm/day. Since Vilas County, Wisconsin, is located at approximately the same average latitude as these Great Lakes, it is estimated that about 30 cm of water would be lost by evaporation over the 185-day period. This represents $< 50\%$ of the annual rainfall to Crystal Lake. Thus rainfall alone seems to be sufficient to offset evaporation suggesting that there might be discharge of lake water to the ground water system. Such a flow out of Crystal Lake was observed in November 1980 (Kenoyer 1980). Although the ground water data is based on preliminary work, it indicates that water may indeed flow from the lake to the ground water during certain times of the year. The spatial and temporal patterns of ground water flow around Crystal Lake presently are being investigated.

Some additional evidence based on chemical analyses suggests that the net contribution of ground water substances to Crystal Lake is small compared to other source inputs. Colman (1979) concluded that rainfall was probably the primary source of water to Crystal Lake. It was suggested that the extremely low concentrations of P and Si in Crystal Lake ($P < 10$ and $Si < 30$ μg/liter) provided evidence that there is little ground water inflow. By comparing Si concentrations in lakes, Colman (1979) argued that higher Si concentrations would be expected in Crystal Lake if there was a large ground water inflow. Stauffer (1981) tends to agree with this reasoning.

Lead-210 also may enter Crystal Lake in surface water runoff. However, Lewis (1977) and Benninger (1978) suggest that soils retain almost all the Pb-210 supplied to them from the atmosphere. The soils most efficient at scavenging Pb-210 exhibit a high organic matter content (Benninger et al. 1975). Since Crystal Lake has a very small, highly permeable, drainage area and is completely surrounded by pine forest, little Pb-210 probably enters the lake from direct surface water runoff. Colman (1979) observed that seepage lakes in general support smaller standing crops of Rn-222 than lakes with larger drainage areas. He states, "Apparently the correlation of larger standing crops of Rn-222 in lakes have larger drainage basins reflects the transport of Ra-226 from the drainage basin soils to the lake sediments."

Based on the preceding observations, the atmosphere seems to provide most of the material input to Crystal Lake. Consequently, a portion of this study concentrated on estimating the atmospheric flux of Pb-210 to Crystal Lake.

SUMMARY OF RESULTS

Based on experimental evidence, the Pb-210 regime in Crystal Lake has been modeled by considering the lake as a two-layer sytem. Transport of particulate phase Pb-210 is more important than diffusion-mediated dissolved phase transport. Standing crops of particulate Pb-210 and SPM were highly variable during the productive stratified period.

It has been hypothesized that some phytoplankters are highly efficient carriers of water column Pb-210 directly to the sediments, while other phytoplankers appear to act more as recyclers of Pb-210. Thus, the specific characteristics of the water column also are a decisive factor in controlling the in-lake cycling dynamics of Pb-210.

The residence time of Pb-210 in dissolved and the particulate phase is greater than a few weeks during the unstratified period. When the lake is more productive (that is, from late spring through the period of thermal stratification) residence times are much shorter, averaging several days. The SML is more dynamic during this period in terms of temporal variations in standing crops of Pb-210. These fluctuations have been ascribed to the activities of primary producers.

The close agreement between atmospheric input and removal of Pb-210 by sedimentation strongly suggests that the atmosphere is the principal source of unsupported Pb-210 to Crystal lake. The mean in-lake flux of Pb-210 was estimated to be 1.77 dpm/cm^2/yr. However no direct relationship was found between supply and removal of Pb-210 over short time intervals due to non-steady-state processes.

Plankton blooms and fall turnover are important events for removing Pb-210 from the water column. The period immediately following ice-out also may be important in this regard. Large deviations from steady-state occur at these times. The system as a whole, however, appears to be in steady-state with respect to input and removal of Pb-210 on a time scale of about 1 yr.

SECTION 10

DYNAMICS OF Po-210 IN THE WATER COLUMN

INTRODUCTION

This is a brief discussion of the Po-210 regime in the water column of Crystal Lake. Based on Po-210/Pb-210 disequilibria, some of the differences in the geochemistries of these isotopes are delineated. A more detailed description of Po-210/Pb-210 particulate phase disequilibria is given in Section 11 to complement the present discussion.

Po-210/Pb-210 DISEQUILIBRIA IN THE WATER COLUMN

The whole lake inventories of dissolved and particulate phase Po-210 have been calculated the same way as Pb-210 (Section 8) and are shown in Table 22. On the average, Po-210 activities are 25% less than activities of Pb-210 in Crystal Lake. On one occasion the inventories Po-210 and Pb-210 were equal. This occurred in the late fall just after turnover (27 October 1979). The "apparent" secular equilibrium is further evidence suggesting conditions in the lake were near steady-state at this time.

TABLE 22. WHOLE LAKE INTEGRATED Po-210 PROFILES (x 10^{-8} DPM)

Date	Dissolved	Particulate	Total
	1979		
5 June	1.20	2.38	3.58
23 June	0.46	2.28	2.74
11 July	0.39	1.67	2.07
16 August	0.57	2.09	2.65
1 September	0.48	1.83	2.32
22 September	0.66	1.96	2.62
13 October	1.07	2.15	3.23
27 October	0.88	2.50	3.39
	1980		
10 May	0.68	2.01	2.69
7 June	0.63	1.31	1.94

Standing crops of dissolved and particulate phase Po-210 were calculated in a manner analogous to that for Pb-210 and are presented in Table 23. In general, the change in standing crop of Po-210 is correlated positively with changes in standing crop of Pb-210. However, this relationship is not adhered to rigorously. Due to the rapid removal of Pb-210 from the water column and the short radioactive half-life of Po-210, the mass balance model developed in Section 9 for Pb-210 is not directly applicable for Po-210. In addition, there was rarely a net loss of Po-210 from the lake.

On the basis of Po-210/Pb-210 disequilibrium in the water column a general picture of the Po-210 regime in Crystal Lake can be developed. The lake is still considered as a two-layer system, but the time resolution of the model is extended to several months. For the purposes of the discussion, the behavior of Po-210 is contrasted for the two time periods. The first interval from 5 June to 22 September 1979 is essentially the stratified period (the productive period). The second interval is termed the unproductive period and extends from 22 September 1979 to 7 June 1980.

For each of these periods the assumptions are made that steady-state conditions can be used to describe the mass balance of Po-210. Based on knowledge of the geochemical regime of parent Pb-210 in Crystal Lake (Section 9), this assumption is probably reasonable for a time period of several months. A material mass balance for dissolved and particulate Po-210 in each of the layers is:

$$\frac{dN_{Po}}{dt} = 0 = I + \lambda_{Pb}N_{Pb} - \lambda_{Po}N_{Po} - RN_{Po} \qquad (19)$$

where:

I = the supply rate from the atmosphere
N = the number of atoms
λ = the radioactaive decay constant
R = the net removal rate by all processes other than radioactive decay.

R is called the "rate constant," and the reciprocal of R is customarily referred to as the "residence time (τ)." The atmospheric flux of Po-210 is <10% that of Pb-210 (this study). The principal source of Po-210 in Crystal Lake is, therefore, from decay of water column Pb-210. If I is neglected as an approximation, Eq. (19) can be rewritten as:

$$RN_{Po} = \lambda_{Pb}N_{Pb} - \lambda_{Po}N_{Po}. \qquad (20)$$

Eq. (20) states that the removal of Po-210 from the water column must be balanced by production of Po-210 from *in situ* decay of Pb-210 and loss of Po-210 by radioactive decay.

TABLE 23. DISSOLVED AND PARTICULATE PHASE STANDING CROPS OF Po-210 (DPM/CM^2) IN CRYSTAL LAKE. THE TOTAL STANDING CROP IS EXPRESSED AS THE SUM OF DISSOLVED AND PARTICULATE PHASES

Date	Depth interval (m)	Dissolved	Particulate	Total
		Surface Mixed Layer		
5 June 1979	0 to 10	0.039	0.083	0.122
23 June 1979	0 to 6	0.011	0.047	0.058
11 July 1979	0 to 6	0.008	0.030	0.038
16 August 1979	0 to 8	0.013	0.058	0.071
1 September 1979	0 to 8	0.010	0.041	0.051
22 September 1979	0 to 10	0.015	0.052	0.067
13 October 1979	0 to 10	0.035	0.072	0.107
27 October 1979	0 to 10	0.031	0.089	0.120
10 May 1980	0 to 10	0.025	0.067	0.092
7 June 1980	0 to 10	0.024	0.043	0.067
		Deep Layer		
5 June 1979	10 to 21	0.041	0.071	0.112
23 June 1979	6 to 21	0.019	0.103	0.122
11 July 1979	6 to 21	0.017	0.087	0.104
16 August 1979	8 to 21	0.026	0.079	0.105
1 September 1979	8 to 21	0.027	0.091	0.118
22 September 1979	10 to 21	0.038	0.097	0.135
13 October 1979	10 to 21	0.038	0.071	0.109
27 October 1979	10 to 21	0.027	0.071	0.098
10 May 1980	10 to 21	0.018	0.066	0.084
7 June 1980	10 to 21	0.013	0.045	0.058

Rearranging Eq. (20) in terms of the residence time τ and expressing Po-210 and Pb-210 as activities:

$$\tau_{Po} = (1/\lambda_{Po})[A_{Po}/A_{Pb}]/(1 - A_{Po}/A_{Pb})] \qquad (21)$$

Eq. (21) says that if we know the activity ratio Po-210:Pb-210, the residence time of Po-210 can be calculated. The activity ratios Po-210:Pb-210 have been calculated and averaged to obtain mean values for dissolved and particulate phases. These ratios are shown in Table 24 for the productive and unproductive periods. The activity ratios were calculated based on the standing crop estimates of Pb-210 and Po-210 presented in Tables 14 and 22, respectively.

TABLE 24. MEAN ACTIVITY RATIOS Po-210:Pb-210 AND RESIDENCE TIMES OF Po-210 (τ_{Po}) IN CRYSTAL LAKE BASED ON EQ. 21 FOR THE PRODUCTIVE (5 JUNE TO 22 SEPTEMBER) AND UNPRODUCTIVE (22 SEPTEMBER 1979 TO 7 JUNE 1980) PERIODS

Interval	SML		DL	
	Dissolved	Particulate	Dissolved	Particulate
		$A_{Po}:A_{Pb}$		
Productive	0.50	0.59	0.74	0.81
Unproductive	0.73	1.15	0.71	1.07
		τ_{Po}(yr)		
Productive	0.6	0.8	1.6	2.3
Unproductive	1.5	4.2	1.3	8.4

The activity ratio Po-210:Pb-210 averaged 0.66 in the whole lake during the productive stratified period. An activity ratio around 0.5 is common for productive surface ocean water (Thomson and Turekian 1976). The subequilibrium activity of Po-210 relative to Pb-210 has been attributed to preferential removal of Po-210 by marine plankton (Shannon et al. 1970, Bacon et al. 1976). The same mechanism is postulated to account for Po-210 deficiencies in Crystal Lake. The dissolved phase was slightly more depleted than the particulate phase, suggesting that dissolved Po-210 was readily scavenged by plankton.

During the unproductive period, dissolved deficiencies of Po-210 were not as great as during the productive season. The dissolved phase activity ratio increased nearly 50% in going from a value of 0.50 in summer to 0.73 during the unproductive period. This increase in the activity ratio is most likely a function of the decreasing intensity of biological activity. The effect of the biological community on the activity ratio is most evident in the SML. In the DL the dissolved deficit was temporally invariant remaining at a level about 25% lower than equilibrium with Pb-210 activities.

The dissolved phase deficiencies of Po-210 in Crystal Lake are most likely maintained by interaction with particulate phase animate and inanimate material. These interactions with the particulate phase apparently are a function of particle type and concentration of suspended particulate matter. The intensity of these interactions is reflected in the residence time of Po-210 in dissolved and particulate phases. These residence times were calculated using Eq. (21) and are presented in Table 24.

The residence time of Po-210 in dissolved and particulate phase is of the order of several years in Crystal Lake. One exception to this was in the SML during the productive summer season. A mean residence time of 0.6 yr was estimated for dissolved Po-210 during this period. This is the same residence time of dissolved phase Po-210 as in productive surface ocean water (Shannon et al. 1970, Nozaki and Tsunogai 1976, Thompson and Turekian 1976, Bacon et al. 1976).

The residence time of Po-210 in particulate phase is about 0.11 yr in the surface ocean (Bacon et al. 1976). In the SML of Crystal Lake the residence time of Po-210 in particulate phase averaged 0.8 yr during the productive period indicating that Po-210 is not removed as efficiently from the SML of Crystal Lake as it is from the surface ocean. It also is evident that Pb-210 is stripped from the water column of Crystal Lake much faster than Po-210. The residence time of Po-210 in particulate phase is on the average 16 times longer than that of Pb-210. If the assumption is made that Pb-210 is removed from the SML primarily by plankton, then plankton are either less efficient at removing Po-210, or Po-210 is not extensively associated with plankton. The correlation of the low residence times of Po-210 with the period of stratification suggests that the cycling of Po-210 is coupled with the activities of plankton.

The residence time of Po-210 in the particulate phase is up to six times longer than in the dissolved phase. This relatively long residence time in the particulate phase--compared to dissolved phase--suggests that Po-210 is extensively recycled in the lake. A significant difference exists between the recycling efficiency of Po-210 and Pb-210. Lead-210, unlike Po-210, has a mean life in the water column of $\leq$100 days. If the overall mean residence time in the lake is 0.20 yr for Pb-210 and 2.6 yr for Po-210, then Po-210 is recycled approximately 13 more times than Pb-210 before removal from the water column. This result is consistent with the behavior of Po-210 and Pb-210 in the surface ocean where 67% of the Po-210 removed from the mixed layer is recycled in the thermocline region and <5% of the Pb-210 is recycled (Bacon et al. 1976).

Broecker et al. (1973) have estimated that each P atom in the mixed layer of the ocean is reused about 10 times before being removed to depth. Such behavior is typical of nutrient elements required by primary producers. The apparent reuse of Po-210 in the water column of Crystal Lake suggests that Po-210 is cycled in a manner analogous to nutrient elements. Kharkar et al. (1976) have postulated the same recycling mechanism is operating for Po-210 in the surface ocean. However, this does not seem to be the case for Pb-210 in Crystal Lake or the surface ocean.

Broecker et al. (1973) stated, "...each pollutant will differ in the rapidity of uptake and the degree to which it is released as a result of the oxidative reactions taking place in animals and bacteria." It was suggested that Th-228 represented an extreme case of rapid irreversible biological uptake since it is removed from the surface ocean by each generation of plant matter. The behavior of Pb-210 in Crystal Lake indicates that it may represent an extreme case of plankton removal. Polonium-210 may lie at the other end of the removal spectrum by being extensively recycled in the water column. This hypothesis is supported by the fact that these nuclides are concentrated to the same extent in plankton from Crystal Lake (at least in mid-summer plankton) but are removed from the water column with vastly different efficiencies.

The distribution of Pb-210 and Po-210 in the lake is, therefore, dependent on the specific biological, physical, and chemical processes disrupting equilibrium between them. The resulting Po-210/Pb-210 disequilibrium in the water column of Crystal Lake demonstrates the selective partitioning of these genetically coupled nuclides between solution and suspended particles. In addition, the disequilibrium depicts the differential removal of the nuclides from the water column. Part of the Po-210 deficiency is caused by direct removal of Po-210 which is most likely transported in particles of biogenic origin as exemplified during the stratified period by the large sedimentation of Po-210 (Section 7). As the lake became less productive the flux of Po-210 decreased by a factor of >10.

Some of the Po-210/Pb-210 disequilibrium is, however, attributed to the short residence time of Pb-210 in the water column compared to the time necessary to establish secular equilibrium with Po-210 (0.5 yr). If Pb-210 is removed with an average residence time of 0.20 yr, then Po-210 would only attain the point of about 50% secular equilibrium with Pb-210 indicating that the selective rapid removal of Pb-210 probably accounts for a portion of the Po-210/Pb-210 disequilibrium.

The effect of the Pb-210 removal on supported Po-210 activities is most pronounced during the productive season where the residence time of Pb-210 is <0.1 yr. During the less productive months the residence time of Pb-210 is nearly adequate to assure equilibrium with Po-210. Figures 9 to 18 show that Po-210/Pb-210 disequilibrium was greatest during the productive period. As fall approached and the lake became less productive, Po-210 and Pb-210 moved closer toward equilibrium. A slight excess of Po-210 appeared in the particulate phase, but this was insufficient to balance the dissolved deficit. Even under the seemingly tranquil conditions existing after fall turnover, Po-210 was still exiled from Pb-210. Since the residence time of Po-210 in the lake is much greater than its radioactive half-life, most of the Po-210 probably decays in the water column and never reaches the sediment.

SUMMARY

The life of an atom of Po-210 in Crystal Lake can be summarized as follows. Polonium-210 beings its life after *in situ* decay of Pb-210. It immediately enters an exhaustive recycling scheme which is mediated biologically. A portion of the Po-210 is removed from the cycling process by sinking biogenic debris. This stripping action is most effective in removing Po-210 during the productive season.

A large fraction of the Po-210 remains in the water column and continues to be cycled until it finally decays to stable Pb-206. If Pb-206 behaves chemically similar to Pb-210 in the lake, it will be removed to the sediments within 1 yr.

The efficient recycling mechanism operating in the lake for Po-210 maintains a fairly constant in-lake inventory of Po-210. This inventory varies by about 20%; Pb-210 inventories vary by almost 30%. The difference in the behavior of Po-210 and Pb-210 in Crystal Lake is dramatically illustrated by variations in the residence times of these nuclides. The residence time of Po-210 varies by a factor of about 20, whereas the residence time of Pb-210 fluctuates by a factor of >300.

SECTION 11

A CLOSER EXAMINATION OF PARTICULATE PHASE TRANSPORT

INTRODUCTION

Most material in the water column is removed by deposition of particulate matter. Therefore, it is important to determine not only the rate of deposition but also to understand the mechanisms facilitating particulate phase removal. This section explores particulate phase transport of Pb, Pb-210, and Po-210 in Crystal Lake by examining isotopic ratios in various particulate phase compartments.

FRACTIONATION OF Pb AND Pb-210

One way to discern whether Pb and Pb-210 have similar mobility in the environment is to determine the ratio Pb-210:Pb in various trace metal compartments and follow the value of the ratio through a particular system. An attempt to do this has been made with regard to Crystal Lake. The Pb-210:Pb ratio is shown in Table 25 for various phases which supply or transport metals in this oligotrophic lake system.

TABLE 25. FRACTIONATION OF Pb-210/Po-210 AND Pb-210/Pb AMONG VARIOUS PHASES TRANSPORTING METALS IN CRYSTAL LAKE

	Pb-210:Po-210, Atom ratio	Pb-210:Pb, dpm/mg
Rain	1,500	2,705
Aerosol	135	901
SPM		
Stratified	80	NA[a]
Unstratified	56	NA[a]
Sediment trap		
Stratified	48	726
Unstratified	79	926
Sediment (0 to 4 cm)	NA[a]	658
Plankton	51	155

[a] NA is not available.

Most of the fractionation of Pb and Pb-210 is conserved from the source aerosol to suspended material in the lake suggesting that Pb and Pb-210 move similarly through the lake. The ratio, however, decreased by a factor of 5 from suspended material to plankton. This decrease is primarily caused by the concentration of Pb-210 (dpm/g) in plankton being about seven times less than it is in suspended matter. Consequently, the concentration of Pb in each of the phases must be about the same.

Several hypotheses can be invoked to describe the observed separation of Pb and Pb-210 including: 1. Pb is in a more available form for active or passive uptake by plankton, including differential aerosol solubility of Pb and Pb-210; 2. there is preferential concentration of Pb by plankton; and 3. Pb-210 is eliminated preferentially by plankton lowering the body burden concentration of Pb-210 over that of Pb. Unfortunately the experimental data presented sheds little light on the reason for the apparent higher concentration factor of Pb in plankton. Detailed research concerning the uptake and transport of metals by plankton is needed to determine if plankton selectively affect the geochemical regimes of Pb or Pb-210 to different degrees.

FRACTIONATION OF Pb-210 AND Po-210

Some insight can be obtained into the particle types which transport Pb-210 and Po-210 in the water column by looking at the atom ratio Pb-210:Po-210 in the particulate phase. A change in the value of the ratio demonstrates fractionation between Pb-210 and Po-210 (Table 25). An atom ratio of 59 indicates the presence of secular equilibrium activities between Po-210 and Pb-210.

It is interesting to note that the atom ratio decreases steadily from atmospheric fallout to plankton. The large value of the ratio in aerosol and rain is consistent with the extreme departure of Pb-210 and Po-210 activities in the atmosphere (Section 8). Once Pb-210 enters the lake from the atmosphere the fractionation of Pb-210 from Po-210 is not readily apparent due to the fact that the principal source of Po-210 in the lake is *in situ* decay of Pb-210.

The atom ratio decreased in SPM from a value of 80 during the stratified period to 56 for the unstratified period. This near equilibrium atom ratio during the unstratified period is caused by a slowing in the removal rate of Pb-210 from the water column. The longer residence time of Pb-210 in the lake allowed the development of a higher supported Po-210 inventory. The averge particulate phase concentration of Po-210 rose from 95 dpm/g in the stratified period to 167 dpm/g during the unstratified period, while Pb-210 was essentially invariant, averaging 125 dpm/g.

During the stratified period the average atom ratio Pb-210:Po-210 was 80. The material collected in the sediment traps, however, exhibited a ratio of 48 which is essentially the same as plankton, i.e., 51. If the sediment traps sampled the downward flux of material in a representative fashion, then plankton apparently aided the deposition of Pb-210 and Po-210 during the productive period. Since the major part of the deposition of Pb-210 and Po-210 was associated with plankton blooms, most of the downward net flux of the nuclides during the productive stratified season is accounted for by this transport mechanism; specifics of the deposition events are unknown, but it appears that the effectiveness of the removal of their nuclides is dependent on the specific biological community involved. Overall, Pb-210 seems to be removed more effectively than Po-210 by biological pathways. However, this is probably not the case for Pb-210 and Po-210 during the unproductive period owing to residence times of 10 to 100 times longer in the water column.

From mid-August until the end of October there was a steady increase in the inventory of Po-210 in the lake (Table 23 and Figure 27). This increase was ascribed previously to the attendant increase in the residence time of Pb-210. Another factor which contributed to development of a higher Po-210 inventory was the separation of Po-210 from Pb-210 in the particulate phase. This point is best illustrated by examining Figure 27 where the activity ratio Po-210:Pb-210 and inventories of Pb-210 and Po-210 are plotted as a function of time. During the more productive summer months the activity ratio is about 0.8. At the time of fall turnover the total activity ratio peaked at about 1.5 primarily due to a rapid increase in the particulate phase ratio (i.e., particulate ratio = 2.34 and dissolved ratio = 1.45). The dissolved/particulate phase inventories of Pb-210 and Po-210 shows the lowest particulate Pb-210 inventory coincides with fall turnover. Particulate phase Po-210 exhibited the opposite trend from Pb-210 and increased at this time. The data clearly indicate that particulate phase Pb-210 and Po-210 reside on different particle types. An exception is plankton where they are present at about the same concentration.

Although the concentrations of Pb-210 and Po-210 in plankton are similar, some obvious disparity exists with regard to biological cycling of the nuclides in Crystal Lake. The lowest activity ratio is 0.6 which occurred in mid-June during the early summer plankton bloom. This low activity ratio is due largely to the 62% decrease in the standing crop of dissolved Po-210 between June 5 and June 23 (Figure 27). In contrast to Po-210, the standing crop of dissolved Pb-210 decreased only 18% over this same time period. Particulate phase Pb-210, however, increased 37%; while particulate Po-210 decreased slightly (~ 4%). The data suggest that Po-210 is rapidly scavenged from solution by plankton (phytoplankton?) and preferentially removed from the biomass by fecal pellets of grazing zooplankters. On the other hand, Pb-210 is apparently carried to the sediments most efficiently near the end of the bloom by dead plankton (Section 9).

In summary, atmospheric Pb-210 supplied to the lake during the bloom is intercepted in the SML by plankton. The effect of the plankton on the Pb-210 geochemical regime is to concentrate Pb-210 in the biomass and hold it in the water column. Consequently, the ratio S:I (Table 17) for the June bloom period was 58%.

The effect of plankton on the Po-210 geochemical regime is far different than its effect on Pb-210. Of the total Po-210 removed in the bloom

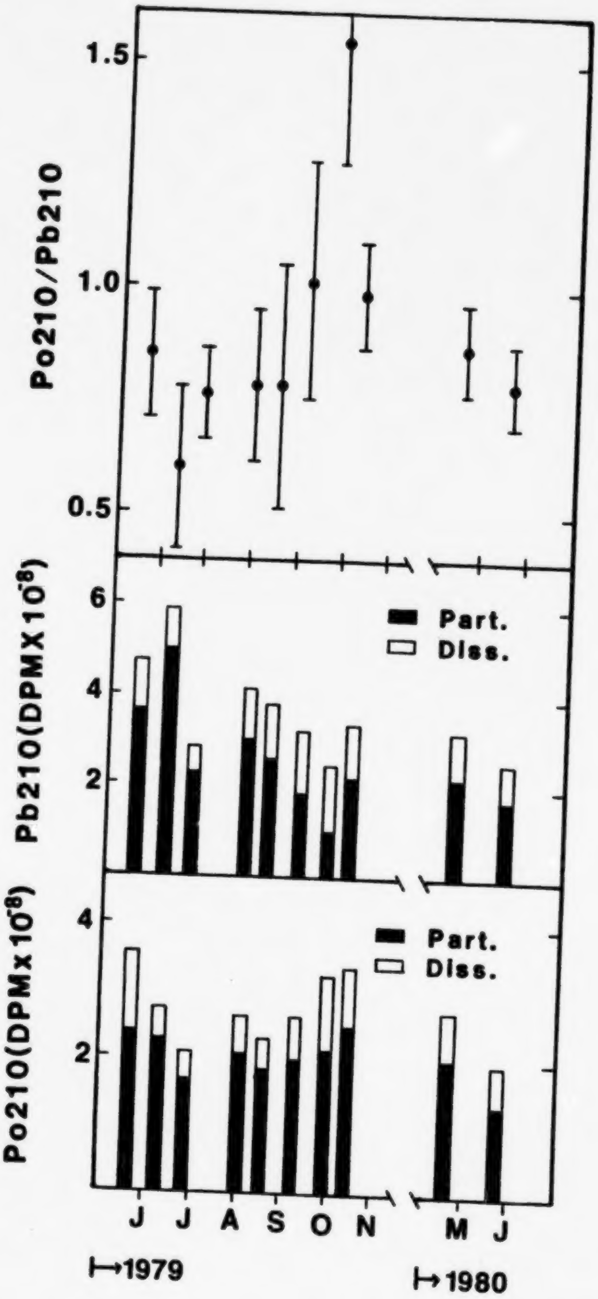

Figure 27. Mean total activity ratios Po-210:Pb-210 and inventories of dissolved and particulate phase Po-210 and Pb-210 in Crystal Lake as a function of time.

period (5 June to 11 July 1979), 56% was removed during the bloom itself and 44% of the removal was associated with bloom die-off. Thus zooplankton fecal pellets appear to be just as important for depositing Po-210 during the bloom as the settling of dead plankton is after the bloom. Fecal pellets of marine zooplankton have been found to contain high concentrations of Po-210 (Cherry et al. 1975).

The fact that Po-210 appears to be scavenged rapidly by phytoplankton and eliminated preferentially in zooplankton fecal pellets suggest that Po-210 flows freely from primary producers to zooplankton. The August plankton data (Table 5) indicates that the concentration of Po-210 is essentially equal in phytoplankton and zooplankton. The concentration of Pb-210, however, is more than three times higher in phytoplankton than in zooplankton. These data indicate that Pb-210 is not passed as freely as Po-210 from primary producers to zooplankton. Consequently, most of the plankton Pb-210 may be in the primary producers making deposition of Pb-210 by fecal pellets of minor importance in removing Pb-210 from the water column. Thus, the increase of particulate phase Pb-210 during the bloom was related to the growth of the biomass of primary producers.

The fate of Pb-210 and Po-210 in the water column during the mid-August plankton bloom was apparently not short-circuited as abruptly in the June bloom. It was suggested in Sections 9 and 10 that the dominant plankton during the August bloom might be less effective as the June plankton in removing Pb-210 and Po-210 from the water column. Another factor which may have contributed significantly to the difference in removal efficiency between these periods is the overall plankton biomass associated with each bloom. Even though the experimental data indicates that the biomass was about the same for each bloom. For this reason the amount of Po-210 and--to a lesser extent--the amount of Pb-210 removed by the August plankton bloom would be less than for the June bloom. Thus, the varied efficiency of plankton in removing Pb-210 and Po-210 from the water column is a function of interrelated biological, chemical, and physical factors.

AN EVALUATION OF IN-LAKE FLUX ESTIMATES

From the results of the two-layer model for Pb-210 (Section 9) an estimate of the mean flux of Pb-210 for the stratified and unstratified periods was determined. If the particulate Pb-210 flux is estimated by averaging the values of T and S from Table 16, the fluxes are as follows: Stratified 1.99 ± 1.37 dpm/cm^2/yr and unstratified 1.49 ± 0.93 dpm/cm^2/yr. The model based fluxes are not statistically different from the observed sediment trap fluxes at the $\alpha = 0.05$ level (c.f. Table 26). Since the model based fluxes are not significantly different than the trap based fluxes, the traps apparently provided an unbiased estimate of the Pb-210 flux (i.e., the trapping efficiency was 100%). However, the trapped material is not related to the membrane-filtered material in a simple fashion (Brewer et al. 1980).

TABLE 26. EVALUATION OF TRAPPING EFFICIENCIES. CONFIDENCE LIMITS FOR THE MEAN WERE CALCULATED AT THE 95% LEVEL. UNITS ARE FOR Pb-210 AND Po-210, AND μg/cm^2/yr FOR Al AND Pb

		Model Estimate	Trap Estimate	Trapping Efficiency (%)
Pb-210	Stratified	1.99 ± 1.37[a]	2.28 ± 0.44	100
Pb-210	Unstratified	1.49 ± 0.93[a]	1.15 ± 0.35	100
Po-210	Stratified	0.40 ± 0.36[b]	0.94 ± 0.22	235
Po-210	Unstratified	0.009 ± 0.02[b]	<0.1	-
Al		11[c]	10 ± 2	100
Pb		1.0[c]	2.1 ± 0.8	100

[a] Model estimate is average of T and S (Table 16).
[b] Based on changes in total standing crop (Table 23).
[c] Based on mean wet and dry atmospheric deposition (Table 12).

The mean in-lake flux of Pb-210 can be calculated using the values of T and S from Table 16 and the observed trap fluxes (Table 6). The in-lake mean fluxes are:

	Pb-210, dpm/cm^2/yr
Stratified	2.09 ± 0.57
Unstratified	1.40 ± 0.48
Annual mean	1.81 ± 0.50

These data indicate that the annual mean flux of Pb-210 is 1.81 ± 0.5 dpm/cm^2/yr. The in-lake flux of Pb-210 was, of course, greatest during the productive stratified period, i.e., being 15% greater than the annual mean flux. During the less productive unstratified period the flux of Pb-210 was 33% less than it was over the stratified period. In addition, the unstratified flux averaged 23% less than the annual mean flux of Pb-210.

Based on changes in the total standing crop of Po-210 in the SML and DL (Table 23), the in-lake deposition of Po-210 can be estimated for the short time intervals between sampling dates. The mean rate of deposition of Po-210 during the stratified period was 0.40 dpm/cm^2/yr. It is interesting to note that deposition of Po-210 was associated almost exclusively with plankton blooms. Furthermore, for at least half the stratified period the data indicate no net deposition of Po-210.

The sediment trap collections give a mean flux of Po-210 of 0.94 dpm/cm^2/yr, a factor of 2 higher than the flux estimated from the water column data (Table 26). The elimination of fecal pellets by zooplankton which migrated into the traps is responsible for the high rate of Po-210 deposition in the traps. Cherry et al. (1975) conducted a laboratory study to determine elimination rates of Po-210 by zooplankton. The concentration of Po-210 in fecal pellets (38.9 dpm/g) was 16 times higher than in whole zooplankton (2.4 dpm/g). The data suggest that the contribution of numerous fecal pellets to the trapped material (this study) would cause the Po-210 flux to be greatly overestimated. Erickson (1980) found that it was necessary to correct sediment trap estimates of pelagic P deposition in Fish Lake, Wisconsin, to account for P contributions from migrating zooplankton.

It is virtually impossible with present data to estimate deposition of Po-210 during the unstratified period. The flux of Po-210 was certainly not greater than 0.1 dpm/cm^2/yr and may have been as low as 0.01 dpm/cm^2/yr. During the unproductive months Po-210 is lost from the water column primarily by radioactive decay (Section 10).

Using the mean summertime estimates of wet and dry deposition of Al and Pb, trapping efficiency can be estimated. It appears that the traps provided a good estimate of the deposition of Al and Pb (Table 26). Since the trapping efficiencies for Al, Pb, and Pb-210 are about equal (~ 100%), this suggest that atmospherically derived Al-silicates may be a major vehicle transporting Pb and Pb-210 in the lake. However, a plot of the flux of Al against the flux of Pb or Pb-210 for each set of traps shows enough scatter that Pb must be associated primarily with other particle types, likely autochthonous biogenic debris.

In conclusion, the sediment traps appeared to provide a reasonable estimate of in-lake fluxes of Al, Pb, and Pb-210. Sediment traps in general, however, may not yield a satisfactory estimate of flux for elements subject to rapid biological cycling (e.g., Po-210 and P).

SECTION 12

SEDIMENT GEOCHRONOLOGIES OF Pb AND Pb-210

INTRODUCTION

The sediments that accumulate in Crystal Lake reflect material transported to the lake from the atmosphere and the drainage basin. Particles also are produced *in situ* by living organism. Of these material inputs, pollen and planktonic debris compose about 50% of the sedimented material (Twenhofel and Broughton 1939).

Crystal Lake acts as a catchment basin for anthropogenic material along with natural tracers like Pb-210. It has been demonstrated that it is possible to document the rate at which material is input to lake sediments by using Pb-210 radiometric techniques (Krishnaswamy et al. 1971, Koide et al. 1973, Robbins and Edgington 1975). Ideally, a complete and detailed historical record is preserved in the sediment column. By correctly reading and interpreting this geochronological record, the history of material input to the lake can be reconstructed.

Pb-210 GEOCHRONOLOGY

Unsupported atmospheric Pb-210 is delivered primarily in rain to the surface waters of Crystal Lake. Due to a 0.20 yr residence time of Pb-210 in the lake, Pb-210 is conveyed rapidly to the bottom sediments. If the flux of Pb-210 to sediments and the sedimentation rate are constant, the vertical distribution of unsupported Pb-210 should decrease exponentially with depth as a result of radioactive decay during burial (Robbins et al. 1977).

In Crystal Lake the flux of unsupported Pb-210 to the sediments approximately equals its atmospheric supply rate over a time interval of 1 yr (Section 9). A further steady-state assumption is made that material deposition is constant in the lake.

The vertical distributions of unsupported Pb-210 in four cores collected from Crystal Lake are shown in Figure 28. The invariant vertical distribution of Pb-210 in the upper few centimeters of the profiles is ascribed to biological mixing. Evidence for biological mixing of the cores is circumstantial, but chironomid worms and their burrow tubes were observed near the sediment-water interface of each of the cores. The benthic activities of tubificial oligochaetes are known to alter sediment particle distributions to depths as much as 10 cm below the sediment-water interface (Davis 1974).

To determine the sedimentation rate from the Pb-210 distributions, only the apparently undisturbed portion of the profiles can be used. According to Robbins et al. (1977), the distribution of unsupported Pb-210 is:

$$A = A_m \qquad z \leq s \qquad (22)$$

and

$$A = A_m e^{-\lambda(z - s)/\omega} \qquad z > s \qquad (23)$$

where:

A_m is the activity in the mixed zone (dpm/g)

λ is the decay constant of Pb-210 (0.03114/yr)

z is the depth below the sediment-water surface (g/cm^2)

s is the depth of the mixed zone (g/cm^2)

ω is the mass sedimentation rate (g/cm^2/yr).

The solid line annotated on Figure 28 represents the distribution of Pb-210 determined from a least squares fit of the data. Analytical results for these four cores are listed in the Appendix. Since the sediments are apparently very homogeneous, one least squares fit was performed on the entire data set. The values of A, ω, and s given in Table 27 were obtained from a least squares fit of the four Pb-210 profiles.

TABLE 27. SEDIMENTATION DATA FOR CRYSTAL LAKE CORES

Unsupported Pb-210 activity in mixed zone A_m	72.4 ± 7
Unsupported Pb-210 activity initially deposited, A_s	218.8 ± 10
Sedimentation rate, W	0.14 ± 0.02
Sedimentation rate, W'	0.008 ± 0.001
Mixed depth, S	4.0 ± 0.5
Mixed depth, S'	0.32
Age at mixed layer boundary, T'	29
Mixing coefficient, K_b	>5.6

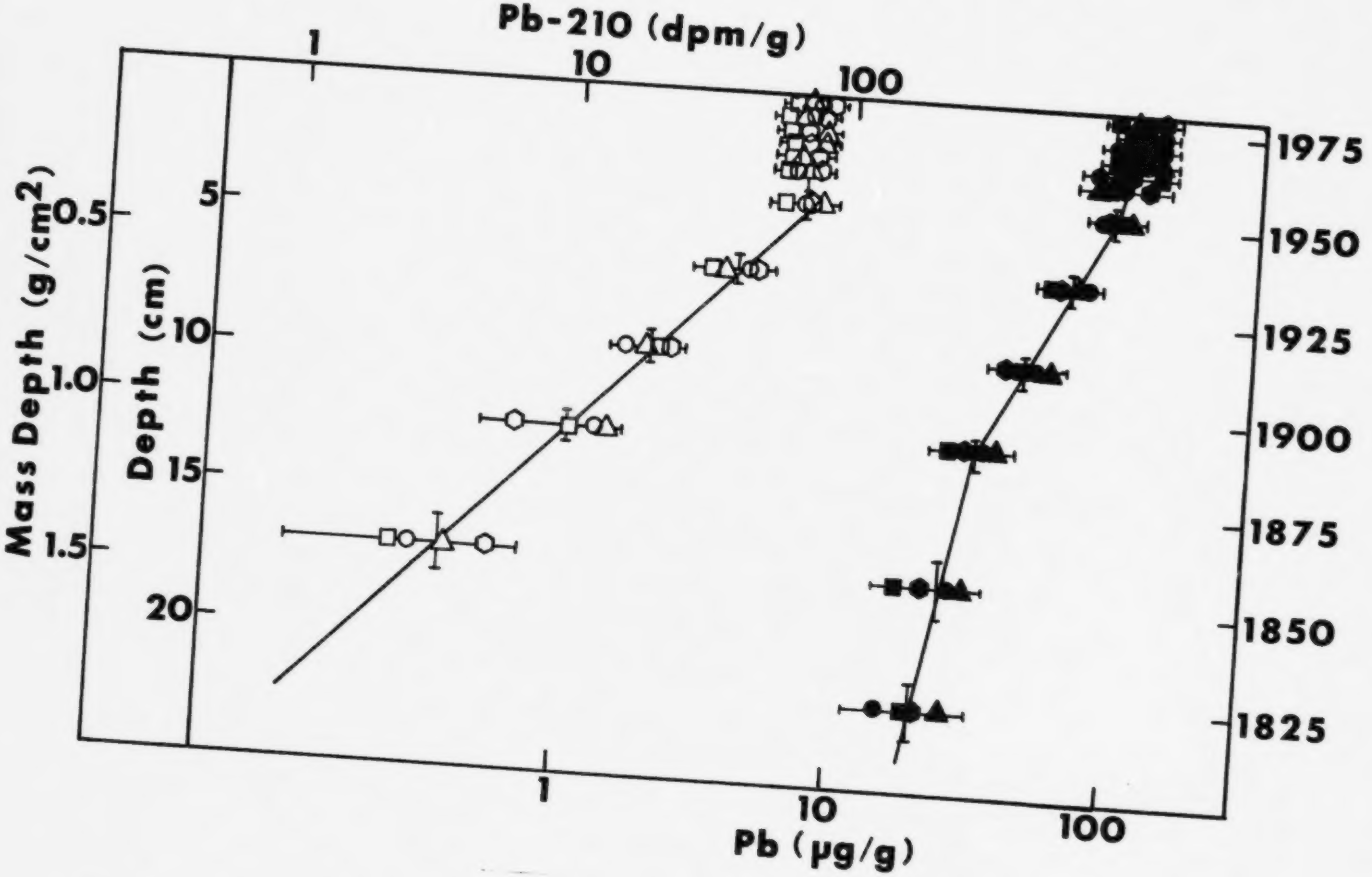

Figure 28. Vertical distributions of Pb (solid) and unsupported Pb-210 (open) in Crystal Lake sediments: ⬡ ⬢ core 1, ○ ● core 2, □ ■ core 3, △ ▲ core 4.

The value of A_m is 72.4 dpm/g while the surface activity, A_s, was predicted to be 218.8 dpm/g. The value of the ratio $A_s:A_m$ is 3.0 for the sediments which shows the effect of rapid mixing on the initially deposited surface sediment activity. Values for the ratio $A_s:A_m$ were reported to be 1.6 and 2.6 for Pb-210 in mixed sediments at two locations in southern Lake Huron (Robbins et al. 1977).

The results of the least squares analysis indicate that the sedimentation rate in Crystal Lake is about 0.14 cm/yr. The rate corresponds to a mass accumulation rate of 8 $mg/cm^2/yr$. The sediment trap experiments indicate the mass flux during the unstratified fall period was 8.1 $mg/cm^2/yr$. Since the mass flux was 15 $mg/cm^2/yr$ during the stratified period, the mass flux during the winter and spring months must average < 8 $mg/cm^2/yr$. The data suggest that the mass flux over 1-yr period varies by a factor of 2 to 3 in Crystal Lake. The annual mean rate of material deposition appears to be about 8 $mg/cm^2/yr$.

The age at the base of the mixed zone can be estimated as $t' = s/\omega$. The age in this case is 29 yr, a little longer than the radioactive half-life of Pb-210 (22 yr). According to Guinasso and Schink (1975) the minimum value of the mixing coefficient for complete homogenization of sediments in the mixed zone is given by: $K_b \geq 10 \cdot \omega \cdot s$. For the Crystal Lake cores $K_b > 5.6\ cm^2/yr$.

The steady-state flux of unsupported Pb-210 to sediments can be calculated using the estimated mass sedimentation rate and the predicted Pb-210 activity at the sediment-water interface:

$$0.008\ g/cm^2/yr \times 218.8\ dpm/g = 1.75\ dpm/cm^2/yr.$$

Based on the statistical uncertainties in the estimated sedimentation rate and the predicted surficial sediment Pb-210 concentration (Table 27), this estimate of Pb-210 flux has an uncertainty of ± 20%.

The mean Pb-210 flux estimated here is in excellent agreement with fluxes estimated from measurements of Pb-210 of 1.79 $dpm/cm^2/yr$ in atmospheric fallout, 1.83 $dpm/cm^2/yr$ in the water column, and 1.86 $dpm/cm^2/yr$ in sedimenting particles.

STABLE Pb GEOCHRONOLOGY

Vertical profiles of the Pb concentration in the four Pb-210 dated profiles are shown in Figure 28. It is evident that the surficial sediment mixing has resulted in a blurred record of the most recent Pb accumulations. The vertical distribution of Pb indicates the mixing extends down to a depth of about 4 cm below the sediment-water interface. This 4 cm mixed depth is essentially the same depth estimated from the sediment Pb-210 distributions.

By extending the apparently undisturbed Pb profile to z = 0 at the sediment-water interface, the surface Pb concentration appears to be 145 μg/g. The average mixed zone Pb concentration is 110 μg/g. For Pb the value of the ratio $A_s:A_m$ is 1.3.

The 1979 concentration of Pb in the sediments has increased approximately eight-fold over the past 150 years. Most of the Pb contamination has occurred during the past 100 years. Shirahata et al. (1980) found a four-fold increase of sediment Pb in a subalpine pond during the last 130 yr. The decreasing ratio Pb-206:Pb-207 in these sediments as the sediment-water interface is approached (1700 to 1972) was attributed to increasing accumulation of non-radiometric anthropogenic Pb. The increasing concentration of Pb in more recent sediments of Crystal Lake most likely reflects anthropogenic Pb input. Most of the Pb pollution probably entered the lake atmospherically.

To examine the spatial surface sediment concentration of Pb, six additional cores were collected on July 31, 1980 (Figure 3 shows sampling site location of cores 6 to 10). The upper 3 cm of the cores were analyzed for Pb. The average surficial sediment concentration was 126 ± 20 μg/g. The data indicate that the spatial deposition of Pb is fairly constant in the pelagic zone of Crystal Lake. It also suggests that the Pb concentration in the Pb-210 dated deep hole cores is not signficantly different than in the six cores. Thus, the deep hole region of the lake provides a relatively unbiased depositional environment from which fluxes of Pb and Pb-210 can be estimated.

The steady-state flux of Pb to the lake is estimated by assuming that the extrapolated surface Pb concentration of 145 μg/g represents present day sediment Pb concentration. The 1979 flux of Pb to the sediments of Crystal Lake is:

$$0.008\ \mathrm{g/cm^2/yr} \times 145\ \mu\mathrm{g/g} = 1.2\ \mu\mathrm{g/cm^2/yr}.$$

This total Pb flux can be divided into a natural and an anthropogenic component by assuming the deep sediments (25 cm) represent the natural (pre-1800) Pb load in these sediments. The average 25 cm concentration of Pb in the sediments is 19 μg/g. The pre-1800 Pb flux is, therefore, 0.2 $\mu g/cm^2/yr$. The present day "excess" anthropogenic Pb concentration in surface sediment is 126 μg/g. The anthropogenic Pb flux is thus 1.0 $\mu g/cm^2/yr$.

Excellent agreement exists between total sediment Pb flux of 1.2 $\mu g/cm^2/yr$ and atmospheric input of 1.0 $\mu g/cm^2/yr$ strongly suggesting that the atmosphere is the principal source of Pb to Crystal Lake. The "excess" is likely due to atmospheric input of automobile Pb.

Edgington and Robbins (1976) have estimated an anthropogenic Pb flux of 1.5 $\mu g/cm^2/yr$ at a mid-lake site (station 17) in Lake Michigan. This location is believed to accumulate Pb primarily from atmospheric fallout. The similar values of the Pb flux in Crystal Lake and at station 17 in Lake Michigan suggest that the deposition of long-range transported aerosol Pb may be 1 to 2 $\mu g/cm^2/yr$ over this general area.

SEDIMENT DISTRIBUTIONS OF Al AND C

The vertical sediment concentrations of Al, organic C, and total C are shown in Figure 29 (Core 1). The distribution of Al shows an inverse trend to C. The inverse fluctuations of Al and C suggest that biogenic contributions (i.e., C) to sediments have varied during the past 150 yr.

The highest sediment C concentrations occurred around the year 1890 (12.5 cm). Prior to this date organic C comprised about 97% of the sediment C. In more recent sediments, this percentage has decreased to approximately 86%. The data indicate that either the C input to the lake is lower now than in the past or the rate of organic matter decomposition has increased dramatically over the past 100 yr.

If the concentration profiles of Al and C are extended from below the mixed layer to the sediment-water interface, the present day concentrations (% dry wt.) are 5.5% for Al, 14.7% for organic C and 17.1% for total C. The average deep sediment concentrations (>15 cm) are: Al - 2.2%, organic C - 19.6%, and total C - 20.2%. On a percent dry weight basis, average Al concentration has increased by approximately the same amount (3.3%) that the C has decreased (3.1%). Over this same 150 yr span, percentage of organic C in the sediments decreased 11% (dry wt.).

The decreasing C content of recent sediments is most likely related to decreased input of C from the drainage area and a subsequent lowering of the lake's biological productivity. Swain (1978) observed an increase in ragweed pollen (*Ambrosia*) in sediments of northern Wisconsin lakes just prior to the turn of this century. The increased pollen input to the sediments suggests that the land surrounding the lakes was logged about this time. The sediment horizon deposited around 1890 in Crystal Lake probably marks extensive land clearing around the lake. The input of terrigenous C most likely accounts for the late 1800 peak in sediment C levels. The input of material appears to have been gradual since no indication exists of a notable change in sedimentation rate.

In addition to increased C input, nutrients were probably washed into the lake. Baker (1974) found that the average P concentration in Crystal Lake was higher 50 yr ago (11 to 18 μg/liter)* than today (<5 μg/liter). The *in situ* production of organic matter from photosynthesis was, therefore, probably higher in the past than today. The newly forested area surrounding the lake apparently has reduced terrigenous input of organic matter and nutrients in Crystal Lake.

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*Data based on archived information of Birge and Juday (1924 to 1942) for the northern Highland Lakes District of Wisconsin. Card files of archived data are available at Steenbock Library, University of Wisconsin, Madison, Wisconsin.

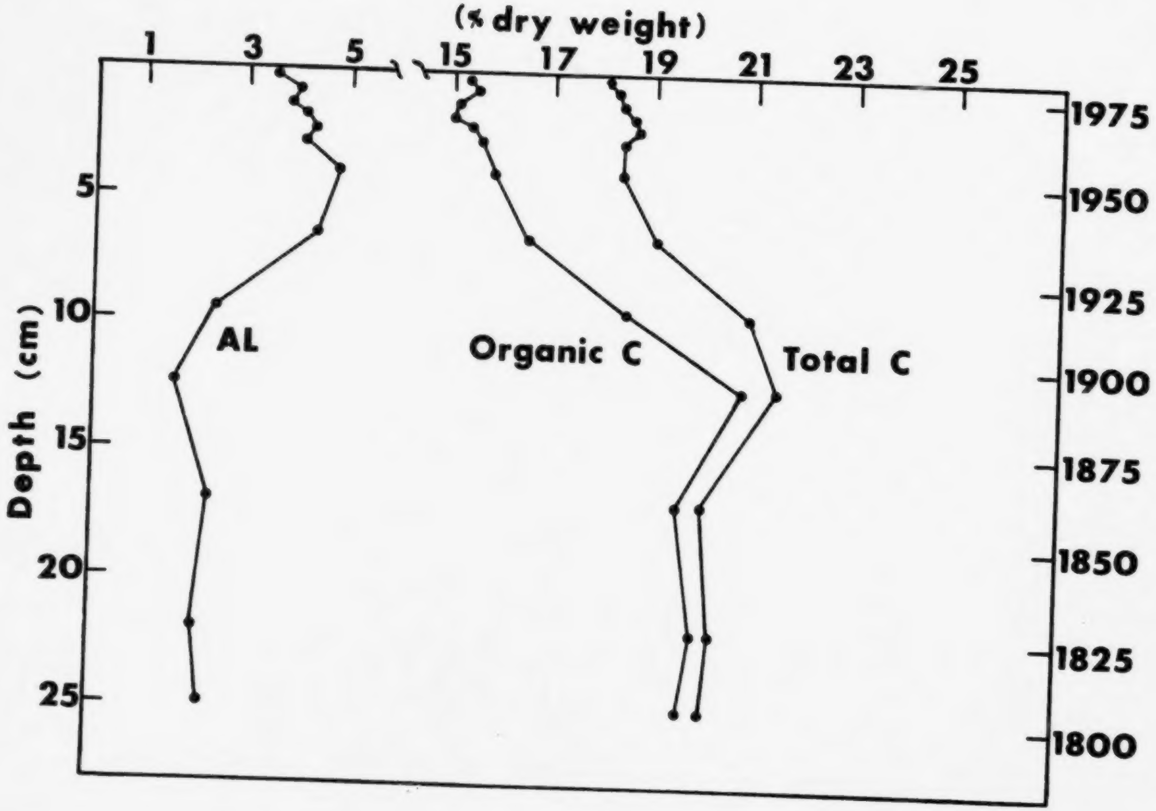

Figure 29. Vertical distributions of Al and C in Crystal Lake sediments (core 1). Dates are based on Pb-210 sedimentation data (See Table 27).

In conclusion, material entering Crystal Lake enters an effective depositional regime and appears to be deposited in the sediments at a rate of 8 mg/cm^2/yr. The rate of deposition has remained fairly constant averaging 0.14 cm/yr despite circumstantial evidence suggesting that the drainage basin contributed more material to the lake in the past than in more recent times. Colman (1979) also concluded that the present material input from the drainage basin to Crystal Lake is small compared to the amount of material delivered by the atmospheric route.

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APPENDIX A

RADIOACTIVE GROWTH AND DECAY CALCULATIONS

ASSUMPTIONS

Friedlander et al. (1964) described the general case of secular equilibrium for determining parent activity based on measured daughter activity. The necessary steps to convert raw counting rates into absolute sample activities are outlined briefly below. In practice these calculations were perfomred on a programmable Hewlett-Packard calculator. For water samples, the assumptions for conversion of raw counting data into sample activity at the time of collection are given by Bacon (1975). These assumptions were modified and are generalized below to apply to all phases sampled here.

1. The activity of Pb-210 supported by Ra-226 decay is negligible compared to unsupported activities of Pb-210 in all phases sampled here except for bottom sediments.
2. The contribution of Pb-210 from decay of Rn-222 equilibrating with stored samples is negligible compared to the Pb-210 activity of the samples.
3. Secular equilibrium is always maintained between the short-lived daughter Bi-210 and parent Pb-210.
4. Po-210 is completely removed from the sample solution by the first plating step.
5. The tracers, Po-208 and stable Pb, behave chemically similar to Po-210 and Pb-210 in the samples.

RADIOACTIVE GROWTH AND DECAY CALCULATIONS

Activities of Pb-210 and Po-210 are represented by Pb(n) and Po(n). Decay constants for Pb-210 (λ_1) and Po-210 (λ_2) are 0.000085/day and 0.0050/day, respectively, corresponding to radioactive half-lives of 22.26 yr and 138.4 days.

Calculation of Pb-210 Activity

1. From the second count determine the Po-210 activity generated after storage of the sample for at least 6 months. This is accomplished by correcting the Po-208 and Po-210 count rates for detector background and simple decay to the time of the second plating:

   Pb(1) = sample cpm - background cpm
   Pb(2) = Pb(1)/exp($-\lambda_2 t_2$)

where:

t_2 is the number of days between plate 2 and the mid-point of the counting interval.

2. The corrected ratio cpm Po-210:Po-208 is multiplied by the activity of the Po-208 spike (dpm) added at plate 2. This gives the Po-210 activity in dpm at the time of the second plating Pb(3).

   Pb(3) = (Pb(2)/Po-208) (dpm Po-208 added)

3. The activity of Pb-210 at the time of the first plating can now be calculated Pb(4), where t_1 is the number of days between the first and second plating.

   $Pb(4) = Pb(3)\ [\lambda_2 - \lambda_1]/\lambda_2\ [\exp(-\lambda_1 t_1) - \exp(-\lambda_2 t_1)]$

4. Finally, the Pb-210 activity at the time of collection is calculated Pb(5), where t_0 is the number of days between the first plating and collection.

   $Pb(5) = Pb(4)/\exp(-\lambda_2 t_0)$

5. Correction is now made for analytical recoveries (R_{Pb}), where R_{Pb} is the fractional recovery of stable Pb.

   $Pb(6) = Pb(5)/R_{Pb}$

6. The reagent blank (dpm) also must be subtracted to obtain the corrected Pb-210 activity at the time of collection Pb(7).

   Pb(7) = Pb(6) - reagent blank

Calculation of Po-210 Activity

1. From the first count determine the activity of Po-210 at the time of the first plating by correcting the Po-208 and Po-210 count rates for detector background and simple decay:

   Po(1) = sample cpm - background cpm
   $Po(2) = Po(1)/\exp(-\lambda_2 t_1)$

   where:

   t_1 is the number of days between plate 1 and the mid-point of the counting interval.

2. The corrected ratio cpm (Po-210:Po-208) is multiplied by the activity of the Po-208 spike (dpm) added at the start of the analytical scheme. This gives the Po-210 activity at the time of the first plating Po(3).

   Po(3) = (Po(2)/Po-208) (dpm Po-208 added)

3. Correction is now made for the reagent blank (dpm) to obtain the corrected Po-210 activity at the first plating Po(4).

   Po(4) = Po(3) - reagent blank

4. Finally, the Po-210 activity is calculated at the time of collection Po(5),

   where:

   t_0 is the number of days between the first plating and collection.

$$Po(5) = \{Po(4) - [\lambda_2/(\lambda_2 - \lambda_1)]\ Pb(4)\ [\exp(-\lambda_1 t_0) - \exp(-\lambda_2 t_0)]\}/\exp(-\lambda_2 t_0)$$

Calculation of Rn-222 and Ra-226 Activity

Extensive calculations are necessary to convert a measured counting rate to an activity of Rn-222 or Ra-226. The calculation procedures have been described previously and are given in detail by Chung (1971) and Colman (1979). For brevity, the calculations are not discussed here.

APPENDIX B

ATMOSPHERIC DATA (1979-80)

TABLE B-1. RAIN DATA (1979)

Collection period	pH[a]	Pb (μg/kg)	Pb-210 (dpm/kg)	Po-210 (dpm/kg)	Pb-210/Pb (dpm/mg)
4 June to 22 June	4.6	5.0	13.6	1.8	2720
23 June to 10 July	4.3	5.4	19.3	ND	3574
11 July to 30 July	4.2	4.6	24.2	ND	5261
31 July to 15 Aug.	4.3	21.7	23.2	ND	1069
16 Aug. to 2 Sept.	4.5	4.9	10.4	0.2	2122
3 Sept. to 21 Sept.	4.4	8.9	13.2	0.7	1483

ND: Not detected.

[a] Model 407A Orion meter equipped with a model 91-02-00 Orion combination electrode.

TABLE B-2. AEROSOL DATA

Collection period (mid-point)	TPS $\mu g/m^2$	Al		Pb		Pb-210		Po-210		Pb-210/Pb dpm/mg	Pb/Al	EF (Pb)
		ng/m^3	$\mu g/g$	ng/m^3	mg/g	dpm/$10^3 m^3$	dpm/g	dpm/$10^3 m^3$	dpm/g			
						1979						
14 June	35	336	9,475	23	0.65	15	425	2	57	654	0.07	438
1 July	25	255	10,243	25	1.00	21	843	ND	ND	843	0.10	625
21 July	30	324	10,929	31	1.06	23	774	28	943	731	0.10	625
8 August	11	177	16,447	18	1.82	20	1,869	ND	ND	1,027	0.11	688
24 August	12	124	11,050	33	2.95	27	2,177	10	806	738	0.27	1,689
12 September	13	164	12,900	21	1.67	21	1,654	9	709	990	0.13	813
2 October	19	254	13,504	17	0.93	18	957	8	426	1,030	0.07	438
2 November	13	69	5,555	22	1.79	18	1,440	12	960	804	0.32	2,001
19 December	15	90	5,935	26	1.71	35	2,318	3	199	1,355	0.29	1,814
						1980						
31 January	6	78	5,625	14	3.76	32	5,161	15	2,419	1,373	0.67	4,190
8 March	6	162	10,919	12	4.39	23	3,898	7	1,186	888	0.40	2,502
19 April	14	258	14,400	14	1.98	20	1,389	ND	ND	701	0.14	876
23 May	26	342	13,249	21	0.80	12	465	3	116	581	0.06	375
Mean	17	203	10,789	21	1.89	22	1,798	10	782	901	0.21	1,313

TABLE B-3. SIZE DIFFERENTIATED AEROSOL DATA

Stage	Al		Pb		Pb-210		Po-210		Pb-210/Pb	Pb/Al	EF
	ng/m^3	µg/g	ng/m^3	mg/g	dpm/10^{6}m^3	dpm/g	dpm/10^{6}m^3	dpm/g	dpm/mg		(Pb)
					1 July 1979						
1	49	11,606	0.9	0.20	216	49	39	9	246	0.02	108
2	39	9,395	1.3	0.33	312	63	71	14	189	0.04	220
3	20	6,719	1.3	0.34	388	101	153	40	296	0.05	316
4	45	11,842	1.9	0.51	3,118	817	ND	ND	1,601	0.04	269
5	16	3,333	4.5	0.94	3,142	652	765	159	693	0.28	1,764
Back up	73	9,352	17.6	2.47	12,987	1,829	ND	ND	740	0.26	1,652
					8 August 1979						
1	26	11,696	0.6	0.27	91	41	249	111	150	0.02	144
2	22	9,643	0.8	0.34	7	3	797	354	9	0.04	221
3	14	7,889	0.8	0.43	323	178	514	284	415	0.06	341
4	14	6,698	1.2	0.54	381	179	2,805	1,317	331	0.08	504
5	40	17,857	2.1	0.93	2,324	1,033	4,708	2,092	1,111	0.05	326
Back up	49	8,933	5.3	3.66	10,060	6,954	2,289	1,582	1,900	0.41	2,562
					23 September 1979						
1	25	7,555	0.2	0.58	151	45	242	72	78	0.08	480
2	33	9,251	0.3	0.88	345	97	ND	ND	110	0.10	595
3	12	4,964	0.3	0.71	410	163	ND	ND	230	0.14	894
4	8	2,838	0.5	1.34	222	80	2,264	815	60	0.47	2,953
5	6	1,773	0.9	3.03	2,201	665	616	186	219	1.71	10,688
Back up	30	4,976	11.3	1.82	12,195	1,973	4,152	672	1,083	0.37	2,289

TABLE B-3. (CONT.)

Stage	Al		Pb		Pb-210		Po-210		Pb-210/Pb	Pb/Al	EF
	ng/m^3	μg/g	ng/m^3	mg/g	$dpm/10^6 m^3$	dpm/g	$dpm/10^6 m^3$	dpm/g	dpm/mg		(Pb)
					2 November 1979						
1	10	7,632	0.3	0.22	121	91	164	125	415	0.03	180
2	13	9,375	0.6	0.83	364	262	168	121	146	0.09	554
3	8	5,886	1.2	0.85	509	371	856	625	437	0.14	903
4	6	3,838	2.1	1.29	864	539	990	617	417	0.34	2,102
5	7	2,669	4.0	1.67	2,788	1,086	5,185	2,019	650	0.63	3,913
Back up	16	2,700	13.6	2.32	17,873	3,041	2,028	347	1,311	0.86	5,374
					19 December 1979						
1	12	11,268	0.5	0.46	69	68	53	52	147	0.04	255
2	12	14,386	1.0	1.19	237	289	7	8	243	0.08	517
3	8	10,962	1.6	2.08	392	523	332	444	252	0.19	1,187
4	6	4,389	2.5	1.91	741	572	600	463	299	0.44	2,721
5	5	2,391	4.4	2.04	2,396	1,121	223	105	549	0.85	5,336
Back up	33	5,255	7.6	1.22	11,940	1,920	2,348	378	1,574	0.23	1,452
					31 January 1980						
1	14	12,827	0.4	0.31	161	80	165	67	258	0.02	151
2	11	11,115	0.8	0.72	234	302	212	183	419	0.07	405
3	8	11,039	0.9	0.94	567	403	357	562	428	0.09	533
4	6	4,822	1.9	2.41	2,157	543	1,561	498	225	0.50	3,126
5	5	2,999	4.7	5.29	5,923	1,099	2,314	2,218	208	1.76	11,031
Back up	27	3,606	7.7	7.64	13,691	2,046	5,394	2,607	274	2.12	13,250

TABLE B-3. (CONT.)

Stage	Al		Pb		Pb-210		Po-210		Pb-210/Pb	Pb/Al	EF
	ng/m^3	µg/g	ng/m^3	mg/g	dpm/10^{6}m^3	dpm/g	dpm/10^{6}m^3	dpm/g	dpm/mg		(Pb)
					8 March 1980						
1	36	10,515	0.3	0.37	154	56	48	79	151	0.04	220
2	27	9,430	0.9	0.96	160	42	278	124	43	0.10	637
3	18	7,548	1.4	1.51	356	216	ND	ND	143	0.20	1,251
4	19	5,251	2.1	2.16	3,315	439	ND	ND	203	0.41	2,573
5	10	2,599	4.0	4.83	2,735	1,433	1,921	912	297	1.86	11,622
Back up	31	5,718	6.7	9.89	11,747	2,003	4,327	1,705	203	1.73	10,817
					23 May 1980						
1	80	3,939	0.4	0.20	108	79	ND	ND	395	0.05	318
2	45	2,590	1.5	0.25	62	59	ND	ND	131	0.10	603
3	23	921	1.7	0.26	56	225	ND	ND	489	0.28	1,765
4	25	2,748	3.2	0.67	79	320	13	54	329	0.24	1,525
5	14	2,500	4.0	1.46	525	2,614	ND	ND	1,791	0.58	3,652
Back up	21	2,187	12.6	2.48	1,497	2,207	ND	ND	890	1.13	7,092

APPENDIX C

CRYSTAL LAKE DATA (1979-80)

TABLE C-1. TEMPERATURE PROFILES (°C)

Depth (m)	6/5/79	6/23/79	7/11/79	8/1/79	8/16/79	9/1/79	9/22/79	10/13/79	10/27/79	5/10/80	6/7/80
0.1	10.7	17.0	23.2	23.1	20.3	20.5	16.7	12.2	9.3	4.8	18.5
1	10.4	17.0	23.1	22.8	20.3	20.5	16.7	12.2	9.3	5.4	18.5
2	10.1	17.0	23.1	22.7	20.3	20.3	16.7	12.2	9.3	5.4	18.4
3	9.9	17.0	22.2	22.5	20.3	20.3	16.7	12.2	9.3	5.4	18.0
4	9.7	17.0	21.8	22.3	20.2	20.3	16.7	12.2	9.3	5.3	17.1
5	9.3	17.0	21.7	22.3	20.1	20.3	16.7	12.2	9.3	4.9	15.6
6	9.1	16.8	20.4	22.3	20.0	20.3	16.7	12.2	9.3	4.7	13.4
7	8.8	14.1	17.5	20.9	20.0	20.2	16.7	12.2	9.3	3.6	12.3
8	8.5	10.8	13.3	17.4	19.8	20.0	16.5	12.2	9.3	2.8	11.7
9	8.3	9.3	11.2	14.8	15.8	18.9	16.5	12.2	9.3	2.4	10.7
10	8.0	8.5	10.5	13.0	13.6	14.9	16.5	12.2	9.3	2.1	9.1
11	7.7	8.1	9.9	11.7	12.2	12.8	15.9	12.2	9.3	2.0	8.7
12	7.5	7.8	9.3	11.1	11.3	11.8	13.4	12.1	9.3	1.7	8.2
13	7.3	7.4	8.7	10.5	10.3	10.9	12.1	12.1	9.3	1.5	7.9
14	7.1	7.0	8.2	10.1	9.9	10.4	11.4	12.1	9.3	1.4	7.7
15	6.7	6.7	7.8	9.7	9.5	9.8	10.9	12.1	9.3	1.3	7.6
16	6.6	6.6	7.7	9.3	9.3	9.7	10.2	12.0	9.3	1.2	7.5
17	6.5	6.6	7.6	9.0	9.0	9.5	9.8	11.3	9.3	1.1	7.5
18	6.4	6.5	7.5	8.7	8.8	9.5	9.6	10.0	9.3	1.1	7.4
19	6.3	6.5	7.4	8.6	8.6	9.5	9.6	9.7	9.3	1.0	7.4
20	6.2	6.4	7.3	8.4	8.4	9.5	9.6	9.3	9.3	0.9	7.3

TABLE C-2. PROFILE DATA FOR SPM, pH, Pb-210, AND Po-210.

Depth (m)	SPM (µg/kg)	pH	Pb-210				Po-210			
			Diss. (dpm/100 kg)	Part. (dpm/100 kg)	Diss.[a] (dpm/100 kg)	Part.[a] (dpm/100 kg)	Diss. (dpm/100 kg)	Part. (dpm/100 kg)	Diss.[a] (dpm/100 kg)	Part.[a] (dpm/100 kg)
5 June 1979										
1	991	6.2	3.6	14.5	3.3	13.5	2.2	7.5	2.0	7.0
5	948	6.1	2.5	13.7	1.7	9.3	4.2	9.2	2.9	6.2
10	1,000	5.9	3.9	9.5	2.0	4.8	5.5	5.6	2.8	2.8
15	1,049	5.9	4.6	5.7	1.4	1.7	3.3	8.9	1.0	2.7
19.5	1,195	5.7	2.8	7.7	0.17	0.46	2.0	7.1	0.12	0.43
23 June 1979										
1	1,024	6.2	3.4	20.8	3.1	19.3	1.7	7.4	1.6	6.9
5	820	6.1	3.7	21.1	2.5	14.3	1.5	7.5	1.0	5.1
10	900	5.9	1.3	8.8	0.65	4.4	1.3	7.9	0.64	4.0
15	1,068	5.7	2.1	10.4	0.63	3.2	0.62	5.0	0.19	1.5
19.5	1,368	5.7	3.2	8.8	0.19	0.53	2.4	8.7	0.14	0.52
11 July 1979										
1	326	5.7	1.9	4.7	1.8	4.4	1.5	3.9	1.4	3.6
4	369	5.9	1.3	8.3	0.94	6.0	0.98	5.2	0.71	3.8
7	609	5.7	2.3	8.3	1.4	5.0	0.51	5.8	0.31	3.5
10	392	5.7	1.0	8.0	0.51	4.0	0.50	5.0	0.25	2.5
15	622	5.7	1.7	6.5	0.53	2.0	2.3	6.0	0.70	1.8
19.5	942	5.5	4.8	10.0	0.29	0.60	2.6	10.5	0.16	0.63

TABLE C-2.(CONT.)

Depth (m)	SPM (µg/kg)	pH	Pb-210				Po-210			
			Diss. (dpm/100 kg)	Part. (dpm/100 kg)	Diss.[a] (dpm/100 kg)	Part.[a] (dpm/100 kg)	Diss. (dpm/100 kg)	Part. (dpm/100 kg)	Diss.[a] (dpm/100 kg)	Part.[a] (dpm/100 kg)
					16 August 1979					
1	983	5.6	3.4	13.4	3.2	12.4	1.5	7.6	1.4	7.0
5	986	5.6	5.0	8.8	3.4	6.0	1.2	6.0	0.84	4.1
8	991	5.6	5.2	8.8	2.9	4.9	1.9	5.8	1.1	3.3
11	917	5.8	0.86	5.8	0.40	2.7	1.5	5.8	0.72	2.7
15	1,089	5.5	2.3	7.4	0.68	2.2	1.8	5.7	0.56	1.7
19.5	1,081	5.8	4.2	9.9	0.25	0.59	4.8	11.3	0.29	0.67
					1 September 1979					
1	503	5.7	4.1	9.0	3.8	8.3	0.95	4.8	0.89	4.5
5	557	5.2	6.5	6.1	4.4	4.1	0.88	4.1	0.60	2.8
8	562	5.9	1.9	9.5	1.0	5.4	1.0	5.5	0.58	3.1
11	616	5.9	2.4	9.2	1.1	4.2	1.5	5.9	0.70	2.8
15	815	5.6	4.0	7.3	1.2	2.2	2.6	8.9	0.79	2.7
19.5	954	5.5	3.3	8.0	0.19	0.48	5.4	11.8	0.32	0.71
					22 September 1979					
1	269	6.0	4.1	4.5	3.8	4.2	1.6	3.9	1.5	3.6
5	293	5.9	4.2	3.9	2.8	2.7	0.84	4.0	0.57	2.7
10	386	5.7	3.6	4.5	1.8	2.3	1.4	4.5	0.68	2.3
12.5	617	5.9	5.3	6.1	2.1	2.4	2.7	5.3	1.1	2.1
15	616	5.8	7.3	14.2	2.2	4.3	4.1	10.0	1.2	3.0
19.5	1,278	5.6	3.4	7.9	0.20	0.47	7.4	22.9	0.44	1.4

TABLE C-2. (CONT.)

			Pb-210				Po-210			
Depth (m)	SPM (µg/kg)	pH	Diss. (dpm/100 kg)	Part. (dpm/100 kg)	Diss.[a] (dpm/100 kg)	Part.[a] (dpm/100 kg)	Diss. (dpm/100 kg)	Part. (dpm/100 kg)	Diss.[a] (dpm/100 kg)	Part.[a] (dpm/100 kg)
13 October 1979										
1	312	5.2	4.8	1.8	4.4	1.7	3.0	7.8	2.8	7.3
5	263	5.4	4.3	3.4	2.9	2.3	3.2	5.7	2.2	3.9
10	209	5.3	4.2	4.2	2.1	2.1	3.1	5.0	1.6	2.5
15	337	4.6	5.9	2.7	1.8	0.81	2.6	5.3	0.78	1.6
19.5	1,179	5.0	1.8	6.4	0.11	0.38	8.6	16.1	0.51	0.96
27 October 1979										
1	486	5.6	3.6	7.4	3.3	6.9	2.6	7.6	2.4	7.0
5	408	5.1	5.0	6.0	3.4	4.1	3.3	9.4	2.2	6.4
10	490	5.7	3.1	6.9	1.5	3.5	2.9	8.4	1.4	4.2
15	463	5.9	4.0	8.6	1.2	2.6	2.6	6.0	0.77	1.8
19.5	522	5.9	3.2	5.6	0.19	0.34	2.4	6.8	0.14	0.41
10 May 1980										
1	468	6.0	4.1	5.9	3.8	5.5	2.6	5.6	2.4	5.2
5	446	5.9	3.7	7.8	2.5	5.3	2.4	6.9	1.6	4.7
10	555	5.8	3.2	7.8	1.6	3.9	1.5	5.6	0.73	2.8
15	787	5.8	2.8	6.2	0.84	1.9	2.1	6.9	0.64	2.1
19.5	943	5.6	3.0	7.1	0.18	0.43	1.9	8.7	0.11	0.52
7 June 1980										
1	110	5.9	3.7	5.3	3.4	4.9	3.6	4.4	3.3	4.1
7	276	5.8	2.0	6.2	1.2	3.7	0.83	3.6	0.50	2.2
14	329	5.8	2.0	5.0	0.68	1.6	1.2	4.5	0.40	1.5
19.5	610	5.6	2.4	6.6	0.14	0.39	1.7	5.7	0.10	0.34

[a] Normalized data concentrations.

TABLE C-3. PLANKTON DATA (DRY WEIGHT)

Collection date (1979)	Depth[a] (m)	Pb (mg/g)	Pb-210		Po-210		Pb-210:Pb dpm/mg	Po-210:Pb-210	Pb-210:Po-210 atom ratio	CF[a] x 10^{-4}	
			dpm/g	pCi/g	dpm/g	pCi/g				Pb-210	Po-210
1 August	0-3	0.23	77.4	34.9	41.3	18.6	337	0.5	110	6.6	5.7
	8-10	0.04	39.0	17.6	24.9	11.2	1,026	0.6	92	3.9	3.7
	17-19	0.01	5.2	2.3	19.0	8.6	371	3.7	16	0.4	1.3
16 August	0-3	0.24	23.9	10.8	36.4	16.4	100	1.5	39	1.4	4.0
	8-10	0.09	4.7	2.1	40.7	18.3	51	8.7	7	0.5	5.4
	17-19	0.10	7.5	3.4	23.9	10.7	79	3.2	18	5.3	1.5
9 September	0-3	0.36	27.2	12.3	24.1	10.9	76	0.9	66	2.1	4.2
	8-10	0.15	16.6	7.5	22.4	10.1	111	1.3	44	1.5	3.2
	17-19	0.20	22.6	10.2	19.0	8.6	113	0.8	70	20.0	1.1

[a]CF = Concentration Factor = ratio of concentration in biota on wet weight basis to that in water.

TABLE C-4. SEDIMENT TRAP DATA

Collection period (1979)	Depth[a] (m)	Mass (mg)	Al (µg)	Pb (µg)	Pb-210 (dpm)	Po-210 (dpm)	Al (µg/g)	Pb (mg/g)	Pb-210 (dpm/g)	Po-210 (dpm/g)
31 July to 31 Aug.	10.5	97	83	20	14.6	7.1	856	0.21	150.5	73.2
	5.5[b]	27	9	11	1.7	3.0	333	0.41	63.7	110.9
	2.5	117	83	13	13.1	18.6	709	0.11	112.0	159.0
1 Sept. to 21 Sept.	10.5	44	50	7	10.9	16.3	1,136	0.16	247.7	370.5
	5.5	59	36	45	8.6	13.0	610	0.76	145.8	220.3
	2.5	75	63	18	13.1	15.7	840	0.24	174.7	209.3
21 Sept. to 26 Oct.	10.5	39	44	7	6.4	2.8	1,128	0.18	164.1	71.8
	5.5	64	73	9	8.6	9.6	1,141	0.14	134.4	150.0
	2.5	86	75	13	11.7	7.7	872	0.15	136.0	89.5

[a] Meters above sediment.
[b] Material lost from trap during recovery.

TABLE C-5. SEDIMENT TRAP DATA: ELEMENTAL AND ISOTOPIC RATIOS

Collection period (1979)	Depth[a] (m)	Pb-210/Pb (dpm/mg)	Po-210:Pb-210	Pb-210/Po-210 atom ratio	Pb/Al	EF[b] (Pb)
31 July to 31 Aug.	10.5	717	0.5	121	0.24	1,506
	5.5	155	1.7	34	1.22	7,639
	2.5	1,018	1.4	41	0.16	979
1 Sept. to 21 Sept.	10.5	1,548	1.5	39	0.14	875
	5.5	192	1.5	39	1.25	7,813
	2.5	728	1.2	49	0.29	1,786
21 Sept. to 26 Oct.	10.5	912	0.4	134	0.16	994
	5.5	960	1.1	53	0.12	717
	2.5	907	0.7	89	0.17	1,083
Mean		793	1.1	67	0.18	1,142

[a] Meters above sediment.
[b] EF = enrichment factor.

TABLE C-6. SUMMARY OF Pb-210 SEDIMENT ANALYSES AND ASSOCIATED EXPERIMENTAL DATA

Section (cm)	Porosity[a]	DBD[a] (g/cm^3)	Mass depth[b] (g/cm^2)	Pb-210 Core 1 (dpm/g)	Pb-210 Core 2 (dpm/g)	Pb-210 Core 3 (dpm/g)	Pb-210 Core 4 (dpm/g)	Core 1 Total C (µg/g)	Core 1 Organic C (µg/g)
0-0.5	0.965	0.052	0.013	84.2	73.8	79.8	64.6	180,333	153,467
0.5-1.0	0.952	0.071	0.053	80.8	70.6	76.2	60.9	182,813	155,847
1.0-1.5	0.951	0.073	0.091	74.0	70.8	85.2	62.9	183,385	150,540
1.5-2.0	0.947	0.078	0.14	71.4	72.8	83.8	68.1	185,781	150,000
2.0-2.5	0.947	0.079	0.18	76.7	65.9	70.8	64.5	186,500	153,963
2.5-3.0	0.946	0.079	0.22	74.1	65.3	77.2	64.3	183,939	154,724
3.5-4.5	0.945	0.080	0.30	74.6	71.5	84.1	61.6	183,281	158,360
6.0-7.0	0.943	0.084	0.55	49.7	47.3	43.0	40.1	165,395	186,949
9.0-10.0	0.941	0.088	0.84	26.5	19.7	27.7	24.8	209,115	184,746
12.0-13.0	0.939	0.090	1.13	9.7	16.4	22.1	15.4	214,706	208,043
16.5-17.5	0.938	0.092	1.54	8.4	6.6	12.0	7.7	200,813	195,028
21.5-22.5	0.936	0.095	2.07	3.2	3.8	8.2	5.4	202,778	198,794
24.5-25.5	0.935	0.096	2.38	3.1	3.7	8.2	5.1	201,143	196,563

[a] Mean porosity and dry bulk density (DBD) of all four cores; $\rho_s = 1.48 \pm 0.22\ g/cm^3$.

[b] At mid-section depth.

TABLE C-7. SUMMARY OF Al AND Pb SEDIMENT ANALYSES

Section (cm)	Al Core 1 (μg/g)	Al Core 2 (μg/g)	Al Core 3 (μg/g)	Al Core 4 (μg/g)	Pb Core 1 (μg/g)	Pb Core 2 (μg/g)	Pb Core 3 (μg/g)	Pb Core 4 (μg/g)	EF[a] (Pb)
0-0.5	35,000	40,049	38,527	34,673	135	115	105	92	20
0.5-1.0	40,187	38,991	36,773	30,616	112	131	120	101	20
1.0-1.5	36,998	47,271	48,104	27,639	129	90	101	116	19
1.5-2.0	41,108	44,151	44,939	40,698	101	113	132	90	19
2.0-2.5	42,614	40,868	48,491	40,733	102	77	92	131	17
2.5-3.0	41,300	38,480	37,688	34,549	121	96	79	87	17
3.5-4.5	47,714	33,589	46,243	41,901	85	80	103	96	16
6.0-7.0	43,402	43,803	48,144	26,426	60	73	69	55	11
9.0-10.0	24,024	36,516	45,369	28,808	38	50	55	45	10
12.0-13.0	16,029	30,744	41,112	27,747	29	33	36	25	6
16.5-17.5	23,572	35,592	41,992	24,809	25	26	29	17	5
21.5-22.5	20,743	25,228	39,867	27,989	21	15	26	19	4
24.5-25.5	22,219	26,624	38,320	27,087	19	18	20	16	4

[a] EF = enrichment factor.